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22 October 1985

USSR REPORT
CHEMISTRY

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ADSORPTION

UDC 541.1:665.521:661.183

CARBON ADSORBENTS FROM SHALE TAR

Kiev UKRAINSKIY KHMICHESKIY ZHURNAL in Russian Vol 51, No 7, Jul 85
(manuscript received 13 Feb 84) pp 714-717

POKONOVA, Yu. V., NAKHINA, L. A. and IVANOVA, L. S., Institute of Physical Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] In order to expand the base of materials from which active carbon can be obtained, experimental studies were conducted with shale tar resulting from thermal processing of shale rock. The polycondensation products were subjected to various methods of carbonization and activation, and analyzed for microstructural parameters and mechanical strength. Studies with the adsorption of CCl_4 , C_6H_6 and CH_3OH demonstrated that pore size could be readily controlled, and that maximum attainable porosity approached $0.30 \text{ cm}^3/\text{cm}^3$. Figures 3; references 5: 4 Russian, 1 Western.
[341-12172]

UDC 66.074.32+541.128.13

DEVELOPMENT OF METHOD FOR MAKING MIXTURE OF OXIDES OF NITROGEN AND CARBON HARMLESS

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHMICHESKAYA TEKHNOLOGIYA in Russian Vol 28, No 6, Jun 85 (manuscript received 11 Jul 83) pp 67-69

PUZANOV, N. S., DANILOV, N. F., KEFER, R. G. and AMIROVA, S. A., Chair of Technology of Inorganic Compounds, Polytechnic Institute

[Abstract] Joint adsorption of the oxides of nitrogen and carbon (N_2O , NO , NO_2 , CO , CO_2) on acid resistant zeolites (mordenite, erinite, clinoptilolite) was studied. Adsorption measurements were made in static and dynamic conditions. The zeolites have a high selectivity relative to NO_2 . At 25°C and component contents of up to 2% by vol., the separation coefficient K_s on mordenite for these systems are: $\text{NO}_2\text{-CO}_2$ 35-45, $\text{NO}_2\text{-N}_2\text{O}$ 80-100,

NO₂-CO 180-220, NO₂-NO 14-30. An adsorption process was developed for separating NO₂ from a gas mixture from blow offs from energy producing installations. Catalytic studies were carried out on 2-3 mm diameter granules of mordenite to obtain fundamental kinetic data for the catalytic decomposition of N₂O and the catalytic oxidation of CO with N₂O. The reaction between N₂O and CO is second order and is limited by the interaction between the adsorbed N₂O molecule and the CO gas molecule. A method is proposed for rendering the gas mixtures harmless with mordenite at 400-450°C. Processing sequence proposed depends on the source of the discharged gas mixture to be treated and its composition. References: 6 Russian.
[342-12886]

UDC 541.13;546.92

EFFECT OF STABILIZATION ON ADSORPTION OF HYDROGEN WITH ELECTRODEPOSITED PLATINUM CATALYSTS

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 26, No 3, May-Jun 85 (manuscript received 8 Feb 84) pp 301-304

GRISHINA, T. M. and MESHCHERYAKOVA, Ye. V., Department of General Chemistry [MSU]

[Abstract] Kinetics of stabilization of electrodeposited platinum electrode-catalysts was studied under conditions of cathodic polarization of electrodes ($I=1\cdot10^{-3}$ A) in a stream of molecular hydrogen and a hot solution with heating up to 80°C (artificial stabilization), aging with storing the electrodes in a sulfuric acid solution (natural aging), and cycling of platinum catalyst electrodes in the potential range of 0.02-1.50 V. Adsorption of hydrogen was investigated by a method of potentiodynamic curves of loading I/E_r in 1 N solution of sulfuric acid. The data of the adsorptive capability of the electrodes with respect to hydrogen indicate that the stabilization process changes the amount and energy of the adsorbed hydrogen and this change is determined by the conditions of stabilization of the electrode-catalysts. The potentiometric curves for different times of stabilization up to 40 hours indicate that as the time is increased to 17 to 40 hours the amount of weakly combined hydrogen exceeds the amount of stably adsorbed hydrogen. The adsorptive capability of artificially stabilized electrodes is decreased with an increase of the time of treatment. This is related to a reduction of the electrode surface. Complete stabilization of the surface of the Pt-electrode occurs after its 30 hour treatment, but the surface of the catalyst is reduced to a third of the initial sample. The surface of the Pt-electrode for stabilization with cycling is reduced and the amount of reduction varies with the conditions of stabilization. The potentials for desorption of hydrogen practically do not depend on the stabilization method of the electrodes and are ~0.13 and 0.26-0.27 V for both freshly prepared electrodes and for stabilized electrodes prepared in various ways. Figures 3; references 7: 5 Russian, 2 Western.
[343-12886]

CATALYSIS

UDC 541.127;541.128.12;546.214

OZONE OXIDATION OF ACETIC ACID SOLUTIONS OF COBALT (II) AND MANGANESE (II)

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 13 Sep 84) pp 487-492

PEREPLETCHIKOV, M. L., TARUNINA, V. N., TARUNIN, B. I. and ALEKSANDROV, Yu. A.

[Abstract] Kinetic studies were conducted on the oxidation of acetic acid solutions of Co(II) and Mn(II) acetates by ozone at 20-48°C. The oxidation of Co(II) to Co(III) was a first order reaction in both cobalt and ozone, with a calculated energy of activation of 44 kJ/mole. The oxidation of Mn(II) to Mn(IV) followed similar parameters, with a rate constant of 5000 L/(mole x/sec) at 20°C. In both cases the entire process consisted of two stages: an initial rapid stage of metal ion oxidation and a slower second stage consisting of acetic acid oxidation to carbon dioxide. The study also demonstrated that Co(III) was a more efficient catalyst for acetic acid oxidation than Mn(IV). Figures 3; references 12: 9 Russian, 3 Western. [331-12172]

UDC 541/128.13:546.881

EFFECTS OF SOLID VANADIUM COMPOUNDS ON DECOMPOSITION OF ORGANIC PEROXIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 3 Aug 83) pp 512-516

BULATOV, M. A., KONONENKO, V. I. and SUKIN, A. V., Institute of Chemistry, Urals Scientific Center, USSR Academy of Sciences, Sverdlovsk

[Abstract] An assessment was made of the catalytic activities of V_2O_3 , VO_2 and V_2O_5 in promoting decomposition of benzoyl peroxide, cumyl peroxide and azobisisobutyronitrile on the basis of rate constants at 70-80°C in bromobenzene. The oxides in question enhanced the rate of radical decomposition of benzoyl peroxide 1.7- to 2.8-fold, and that of cumyl peroxide 600- to 6000-fold. However, they had no effect on the nonperoxide initiator of polymerization azobisisobutyronitrile. The rate increase was

ascribed to the interaction of the peroxides with the vanadium ions on the surface of the oxides. Figures 3; references 13: 10 Russian, 3 Western. [331-12172]

UDC 547(313.2+537)541.64:542.971.2

OLIGOALKYLATION OF BENZENE BY ETHYLENE USING ZIRCONIUM-CONTAINING CATALYTIC SYSTEM

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 21, No 6, Jun 85
(manuscript received 10 May 84) pp 1233-1237

AKHMEDOV, V. M., AKHUNDOV, A. A. and SAMEDOVA, G. F., Institute of Petrochemical Processes imeni Yu. G. Mamedaliev, AzSSR Academy of Sciences, Baku

[Abstract] A catalyst containing zirconium acetylacetonide, ethylaluminum dichloride and an alkyl chloride or bromide was used in production of alkyl benzenes of varying chain lengths from benzene and ethylene. No unsaturated compounds were produced when the ratio of alkyl halide to aluminum compound was 0.67 to 1.25. The molecular mass of the product was independent of ethylene concentration and was somewhat increased by increasing the reaction temperature from 350°K to 413°K. Maximal reaction rate increased with ethylene concentration and decreased with increasing temperature. The reaction mechanism is proposed to include interaction of the zirconium and aluminum containing components of the catalyst to form an active center, chain growth via ethylene oligomerization due to interaction of the active center with ethylene, deactivation and alkylation of benzene by the alpha-olefins which are formed. The fourth step is much faster than the first three. Reaction rate was first order in zirconium and ethylene, with a rate constant which decreased exponentially over time due to deactivation. The deactivation rate constant increased with temperature, with an activation energy of 20.6 kJ/mole. Chain elongation has an activation energy of 4.4 kJ/mole. Figures 2; references 11 (Russian). [336-12126]

HYDROGENATION OF POLY-ALPHA-OLEFINS ON CATALYST WITH SURFACE DISTRIBUTION OF PALLADIUM

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 3, Mar 85 pp 12-13

BERENBLYUM, A. S., KARELSKIY, V. V., MUND, S. L., TSVETKOV, O. N. and
DIANOV, V. F., All-Union Scientific Research Institute for Petroleum
Products

[Abstract] Owing to their rheological properties, poly-alpha-olefine oils (PAOM) are used in a variety of applications. The poly-alpha-olefines that are formed during production of the PAOM have essentially the same physical chemical properties as the PAOM except for the presence of some unsaturated hydrocarbons which must be hydrogenated to render the oil resistant to oxidation. Industrial catalysts, such as nickel-on-kieselguhr and palladium-on-aluminum oxide, do not provide sufficient depth of hydrogenation at the space velocities and pressures employed in the process. In the present work it was found that if the palladium is distributed on the surface of a cusp-shaped carrier particle, the hydrogenation process may be intensified without changing the pressure and space velocity. Figures 4; references 3 (Russian). [308-12765]

REGULARITIES GOVERNING PROPANE DEHYDROGENATION OVER CATALYST IM2201

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 3, Mar 85 p 14

LOZHKINA, V. B., BALASHOVA, V. V. and DOROGCHINSKIY, A. Z., Groznyy
Petroleum Institute imeni M. D. Millionshchikov

[Abstract] The demand for propylene, obtained chiefly by pyrolysis and catalytic cracking, has grown to such proportions that these methods are no longer sufficient, and now it must also be derived by dehydrogenation of propane. In the present work, a study was made of propane dehydrogenation over a fluidized bed of catalyst IM2201, normally used for n-propane dehydrogenation and chosen because of experience acquired in its use. The study was conducted under laboratory conditions with a 30 cm³ charge of catalyst in a 5 cm dia reactor at 400-800 hourly space velocity and 570°-650°C. Samples were extracted for chromatographic analysis at 5 min intervals. Propane dehydrogenation is a highly endothermal reaction, but at high temperatures secondary reactions of propane cracking and coke formation take place. Optimum residence time was 10-20 min; maximum propylene yields were obtained at 630°-640°C at 400 and 800 hourly space velocity with 57-59% and 47-51% (by weight) conversion, respectively. Published indices for catalyst K-5 are not as high, and therefore catalyst IM2201 appears to be promising for propane dehydrogenation. Figures 2; references 6: 3 Russian, 3 Western. [308-12765]

UNIVERSAL ENZYMATIC CATALYST SUITABLE FOR AQUEOUS AND ORGANIC SOLVENTS:
CATALYTIC ACTIVITY AND STABILITY OF ALPHA-CHYMOTRYPSIN INCORPORATED INTO
COLLOIDAL PARTICLES OF POLYACRYLAMIDE

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 283, No 1, Jul 85
(manuscript received 18 Jul 84) pp 136-139

ABAKUMOV, Ye. G., LEVASHOV, A. V., BEREZIN, I. V., academician, USSR
Academy of Sciences, and MARTINEK, K., Moscow State University
imeni M. V. Lomonosov

[Abstract] Studies were conducted on the thermal stability of alpha-chymotrypsin incorporated into colloidal (100-400 Å) polyacrylamide particles, forming a gel solution. Such chymotrypsin preparations were soluble in both water and organic solvents enriched with micelle-forming surfactants. Analysis of thermal inactivation plots (using N-acetyl-L-tyrosine ethyl ester substrate) showed that the native enzyme lost activity at 45°C, whereas the immobilized enzyme retained a high level of activity (ca. 80%) even at 65-70°C. It appears that the method of immobilization of alpha-chymotrypsin can be expanded to encompass other enzymes to prepare biocatalyst preparations soluble in water and organic solvents. Figures 2; references 5 (Russian). [340-12172]

CATALYTIC OXIDATION OF CO IN Pd(II)-Fe(II)-NaNO₂ SYSTEM

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 7, Jul 85
(manuscript received 23 Mar 84) pp 712-714

BELOUSOV, V. M. and PAL'CHEVSKAYA, T. A., Institute of Physical Chemistry,
Ukrainian SSR Academy of Sciences, Kiev

[Abstract] An analysis was conducted on the factors leading to the oxidation of CO to CO₂ in a system consisting of Pd(II) and Fe(II) halides and NaNO₂, since, in the absence of the Pd(II) and Fe(II) salts, NaNO₂ fails to oxidize CO. Analysis of the rate constants of CO₂ formation in the absence and presence of NaNO₂ led to the determination that, in the system in question, Pd(II) functions as a catalyst, and Fe(II) as a cocatalyst. The overall reaction was established as $\text{CO} + 2\text{NaNO}_2 +$

$2\text{HCl} \xrightarrow{[\text{Pd(II)-Fe(II)/Cl}^-, \text{Br}^-]} \text{CO}_2 + 2\text{NO} + 2\text{NaCl} + \text{H}_2\text{O}$. The addition of

$6 \times 10^{-2} \text{ M Br}^-$ increased the rate of the reaction 3- to 4-fold, with a optimal $\text{Br}^-/\text{Cl}^- = 0.06-60$. Figures 1; references 5 (Russian). [341-12172]

INDUSTRIAL TRIALS WITH GO-117 CATALYST IN HYDROREFINING

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 7, Jul 85 pp 39-40

BELYAYEVA, Z. G., NAZAROV, V. I. and KUTLUGIL'DIN, N. Z.,
"Salavatnefteorgsintez" Industrial Association

[Abstract] Long-term trials were conducted with industrial testing of GO-117 catalyst in hydrorefining of diesel fuel and gasoil. Using standard conditions applicable to such operations showed that under operating temperatures of 360°C and a pressure of 0.15 MPa the sulfur concentration was reduced from 1.8% to 0.1%. On the basis of these preliminary results, the 11 month studies showed that GO-117 was more efficient than catalyst AKM in desulfurization.

[345-12172]

UDC 541.128

PHASE DISTRIBUTION IN Al-Ni-Mo CATALYSTS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 7, Jul 85 pp 41-42

MIKHAYLOV, V. I., CHUKIN, G. D., SAMGINA, T. Yu. and NEFEDOV, B. K.,
All-Union Scientific Research Institute of the Petroleum Industry

[Abstract] Light scattering was employed to assess phase distribution in Al-Ni-Mo catalysts following annealing at different temperatures. In a sample annealed at 573°K with 60 wt% NiMoO₄ the surface of the granules consisted largely of the P phase of NiMoO₄, and a small amount of N phase bands (somewhat wider than bands obtained from the N phase of NiMoO₄). Spectra obtained from internal section of cut granules indicated a rapid decrease in the P phase in going from the surface to the interior. The centers of some granules luminesced, indicating weak interactions of nickel molybdates with gamma-Al₂O₃ surfaces. Spectra obtained from different regions of granules annealed at 823°K differed little from one another, showing predominance of the P phase. Figures 1; references 4 (Western).

[345-12172]

CATALYTIC CONVERSION OF 1,1-DIMETHYLHYDRAZINE ON APPLIED PALLADIUM CATALYST

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 26, No 3, May-Jun 85 (manuscript received 5 Feb 84) pp 260-262

RAZUMAYEVA, A. Ye., YEMELYANOVA, G. I. and STRAKHOV, B. V., Department of Physical Chemistry [MSU]

[Abstract] Catalytic conversion of 1,1-dimethylhydrazine (I) on applied iridium catalyst Ir/Al₂O₃ (30% by wt.) was reported recently by the authors in reference 1. Though the catalyst was effective, it was poisoned quickly and could not be restored easily. Because of this and to find a catalyst such as Ir/Al₂O₃ which could be used at moderately high temperatures and have a greater stability, catalytic conversion of (I) on applied palladium catalyst Pd/SiO₂ (0.9% by wt.) was investigated. Mol % composition of the products N₂, CH₄, NH₃, dimethylamine (II) for Ir/Al₂O₃ and Pd/SiO₂ at 100-200°C is given. Mol % of (II) is 69-57 for Pd/SiO₂ and 65-49 for Ir/Al₂O₃ at 100-200°C. Higher temperatures increase the reaction of (I) to N₂ and CH₄ for both catalysts, but Pd/SiO₂ conversion is more selective, for the reaction, of (I) to (II), NH₃ and N₂ for the entire temperature range studied. Evaluation of the kinetic parameters showed the reaction rate constant to be 1.7 mcmol/g·atm·sec at 200°C. Activation energy is 21.5 kcal/mole. Catalytic activity for the palladium catalyst is almost 10 times greater than for the iridium catalyst for the conversion of (I). The calculated values of activity at 200°C are $A_{Ir}=3.4 \cdot 10^{-20}$ and $A_{Pd}=33.4 \cdot 10^{-20}$. Noticeable decrease of catalyst

activity was not observed for the palladium catalyst. For (I) the palladium catalyst is better both in the quantitative ratio and in stability.

References 7: 5 Russian, 2 Western.

[343-12886]

MECHANISM OF FORMATION OF SKELETAL CATALYSTS FROM MULTICOMPONENT ALLOYS BASED ON NICKEL-ALUMINUM

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 6, Jun 85 (manuscript received 3 Feb 83) pp 1388-1392

IKHSANOV, Zh. A., MIKHAYLENKO, S. D., KITAYGORODSKAYA, V. Ya., MAKSIMOVA, N. A. and FASMAN, A. B., Institute of Organic Catalysis and Electrochemistry, KaSSR Academy of Sciences, Alma-Ata; Alma-Ata State Medical Institute

[Abstract] X-ray spectral microanalysis and solution electron microscopy were used to investigate the phase composition and susceptibility to alkali

corrosion of two alloys (mass %): 21% Ni, 11% Mo, 2% Cu, 0.5% Cr, 63.5% Al (I) and 26% Ni, 9% Mo, 4% Fe, 4% Cu, 1% Cr, 56% Al (II). The microstructure of both alloys was polyhedral. Thin sections of the alloys were subjected to 20% KOH solutions for 3-5 min, 20-30 min, and 1.5-2.0 hrs. Alloy I was 100% selective in catalyzing the hydrogenation of 2-ethylanthraquinone. It was intensively attacked by alkali, with Al content falling from 81 to 20 atomic % in 1.5 hr. This alloy showed four distinct regions, two of which were easily attacked. Alloy II showed only an 81% selectivity as a catalyst, but was much more resistant to alkali--apparently due to the presence of such corrosion-resistant phases as Ni_2Al_3 and a Mo-containing N -phase. Similar alloys modified with Ti showed the formation of an alkali-resistant quaternary compound approximately $Ni_4Ti_4Mo_{17}Al_{75}$. If cast under conditions not favoring equilibrium formation of this resistant compound, alloys with both Mo and Ti showed high activity and selectivity in the hydrogenation of 2-ethylanthraquinone. Figures 2; references 11: 6 Russian, 5 Western. [335-12672]

UDC 541.128.34.665.644.2.661.183.6

CATALYTIC ACTIVITY AND ACIDIC PROPERTIES OF COCRYSTALLIZED PHASES OF MORDENITE AND ULTRASIL

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 6, Jun 85
(manuscript received 8 Jul 83) pp 1404-1408

YUSHCHENKO, V. V., TOPCHIEVA, K. V. (deceased), MEGED, N. F. and LIMOVA, T. V., Moscow State University imeni M. V. Lomonosov

[Abstract] The acidic and catalytic properties of a series of zeolites ranging from large-pore N-mordenite through cocrystallized intermediates to fine-pore, high-silica ultrasil were examined. The mineral phases in the cocrystallized samples varied somewhat from the pure minerals, so the results of cracking of n -octane show general tendencies of changes in properties as the phase composition changes. Product yields generally varied with the composition of the catalyst and with the total conversion, although ethane and n -butyl yields were not affected by these parameters. Catalysts with a higher content of N-mordenite tended to isomerize n -octyl cations, so these samples gave a higher yield of iso-butane. They also gave a higher yield of paraffins compared to olefins, as shown in detailed tables. However, the activity of pure N-mordenite fell practically to zero in the course of 240 min, while the activity of a sample with 15% ultrasil stabilized after 180 min. Increasing the ultrasil level gave a progressively lower starting activity level, but the activity level stabilized increasingly more rapidly. The acidic properties of the samples, measured by the thermal desorption of ammonia at temperatures of 100-500° C, was highest for the N-mordenite and lowest for the ultrasil, with intermediate compounds showing intermediate values, but all significantly below the N-mordenite values. Even small amounts of ultrasil apparently screen the N-mordenite phase from ammonia. Figures 2; references 30: 13 Russian, 17 Western. [335-12672]

INFLUENCE OF MEDIUM OF IRRADIATION ON CONDITION OF PALLADIUM DEPOSITED ON SILICA GEL

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 6, Jun 85
(manuscript received 26 Jan 84) pp 1530-1531

KUANYSHEV, A. Sh., KUZEMBAYEV, K. K. and ASUBAYEV, M. K., Institute of Organic Catalysis and Electrochemistry, KaSSR Academy of Sciences, Alma-Ata

[Abstract] Catalyst samples with 4% Pd on silica gel were irradiated with ^{60}Co in hydrogen or oxygen atmospheres. Infrared spectroscopy of CO adsorption was then carried out at pressures of 20-27 kPa. Different spectral bands of differentiate between adsorption on the (100) and (111) crystal faces of Pd. They show that irradiation in a reducing or oxidizing atmosphere leads to structural changes in the active phase, respectively increasing or decreasing the yield on the (111) crystal surface of the Pd. References 8: 1 Czech, 4 Russian, 3 Western.
[335-12672]

CATALYTIC OXIDATION OF GALLIUM ARSENIDE IN PRESENCE OF PLATINUM

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 6, Jun 85
(manuscript received 14 Feb 84) pp 1552-1553

UGAY, Ya. A., ANOKHIN, V. Z. and MALEVSKAYA, L. A., Voronezh State University imeni Leninskiy Komsomol

[Abstract] Polished Pt, positioned parallel to the surface of GaAs at a distance up to 1.5 mm, has a noticeable catalytic effect on its oxidation. Plates of GaAs were treated with concentrated hydrofluoric acid for 20 min, washed with distilled water, and positioned at 0.2 mm from a polished platinum surface in an atmosphere of moist oxygen at temperatures of 470, 490, 510, 520 and 530° C. Portions of the GaAs plates at least 1 cm from the edge of the platinum were used as control samples. The oxidation of the GaAs proceeded 1.5 to 3 times faster in the presence of the Pt and formed a more uniform oxide film. Kinetic parameters were calculated and a table is given. In the presence of the Pt catalyst, the reaction reached a thickness of oxide layer where its rate was diffusion-controlled. Above 490° K, the kinetic curves indicated the active evaporation of arsenic oxide from the growing oxide layer; x-ray analysis indicated the catalyzed samples retain a higher fraction of this component. The energy of activation for catalytic and control samples was calculated at 183 and 335 kJ/mole respectively. Figures 1; references 1 (Russian).
[335-12672]

COAL GASIFICATION

UDC 547.02+662.737.1+665.761.3

COMPOSITION OF NEUTRAL OILS OBTAINED FROM PROCESSING KANSK-ACHINSK BASIN COALS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 7, Jul 85 pp 8-11

PLOPSKIY, Ye. Ya., KIRILETS, V. M., SIDEL'NIKOV, V. N. and UTKIN, V. A.,
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Institute of Catalysis, Siberian Department, USSR Academy of Sciences

[Abstract] Chemical analysis was conducted on neutral oil fractions obtained from Kansk-Achinsk coal by treatment with lower aliphatic alcohols. The supercritical solution under analysis was prepared by treatment with iso-propanol (2.5:1) as the hydrogen donor. Subsequent high-performance liquid chromatography resulted in resolution of the neutral oil component (ca. 50% of supercritical solution) into 5 fractions. Fraction A consisted of normal alkanes ($C_{14}-C_{19}$), with mass spectrometry peaks at $m/e = 113, 183$ and 268 . Fraction B was represented by alkyl derivatives of indane and tetraline, fraction C by naphthalene and its derivatives. Fraction D consisted of low-volatility components not further analyzed, while E was represented by heteroatomic compounds, including cyclohexanol and octanol. Catalytic refining of the neutral oil fraction on catalyst GK-35 yielded light motor fuel with an octane number of 88. Figures 4; references 11: 4 Russian, 7 Western. [345-12172]

ELECTROCHEMISTRY

UDC 669.24'74-154

RELATIVE ELECTRICAL RESISTANCE AND MAGNETIC SUSCEPTIBILITY OF Ni,Mn-ALLOYS AT HIGH TEMPERATURES

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 6, Jun 85
(manuscript received 1 Jul 83) pp 1509-1512

KUDRYAVTSEVA, Ye. D., KONOVALOV, S. V., SINGER, V. V., RADOVSKIY, I. Z.
and GELD, P. V., Ural Polytechnic Institute imeni S. M. Kirov, Sverdlovsk

[Abstract] Finely divided, highly purified Ni and Mn were pressed into tablets (0-70 mass % Mn) and remelted in an induction furnace under an Ar atmosphere. In the range 600-1750° C, the electrical resistance was measured by a method of rotating magnetic fields and the magnetic susceptibility by Faraday's method. At concentrations of Mn over 10 mass %, electrical resistance rose linearly with temperature. Similarly, increasing Mn content generally led to an increase in magnetic susceptibility, with no substantial changes noted on melting, indicating no significant change in near order of the atmos in the liquid phase. Based on data from these measurements, the number of unpaired electrons was calculated. This, in turn, was used to verify the applicability of a Faber-Ziman-Evans model of the electron structure of these metals and their alloys. Figures 5; references 6: 2 Russian, 4 Western.
[335-12672]

UDC 577.3:541.139

INFLUENCE OF WEAK CONSTANT MAGNETIC FIELD ON AUTOOSCILLATING REACTION OF BELOUSOV-ZHABOTINSKIY

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 6, Jun 85
(manuscript received 12 Jul 83) pp 1513-1516

AGULOVA, L. P. and OPALINSKAYA, A. M., Siberian Physico-technical Institute imeni V. D. Kuznetsov, Tomsk State University, Tomsk

[Abstract] The oxidation of malonic acid by potassium bromate in the presence of a catalyst-- Ce^{+3} and Ce^{+4} --oscillates and can be easily tracked photometrically

due to the changing optical density of the mixture. Two quasi-harmonic regimes were investigated, one (nonstationary) near the limit of the region of oscillation and one (stationary) far from this border and showing amplitude fluctuations 2-3 smaller. In the nonstationary regime, in a constant magnetic field of 0.2 to 80 A/m, the amplitude of the oscillations and the amount of fluctuations in amplitude changed relative to control samples. The changes, however, were not reproducible, particularly near the limits of the oscillation region. This was possibly due to changes in the cosmo-geophysical conditions and other transient magnetic fields. In the stationary regime, fluctuations were significantly less and not statistically significant, indicating that magnetic fields act more effectively in regimes near to the limits of oscillation. Figures 1; references 8 (Russian).
[335-12672]

FREE RADICALS

UDC [547.413+547.569.1]:541.114

FREE RADICAL REACTIONS OF 1,1,2-TRICHLOROPROPENE. PART 2. FREE RADICAL
THIYLATION OF TRICHLOROPROPENE BY ARYL THIOLS

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 21, No 6, Jun 85
(manuscript received 23 Feb 84) pp 1159-1165

MARTYNOV, A. V., MIRSKOVA, A. N., VITKOVSKIY, V. Yu. and VORONKOV, M. G.,
Irkutsk Institute of Organic Chemistry, Siberian Department, USSR Academy
of Sciences

[Abstract] The products of the reaction of trichloropropene with three aryl thiols, 4-methylphenyl, phenyl and 4-chlorophenyl, were studied. Gas chromatography of the reaction mixtures revealed products with retention times identical to those of the corresponding beta,beta-dichloro-isopropenylsulphides synthesized by nucleophilic substitution. However, the isolated products possessed different IR and PMR properties from the standards. Some of the products were partially resolved using a different GC method. Production of cis and trans disulfides was also noted and confirmed by GC-mass spectrometry. The unresolved main peak appears to contain the three sulfide isomers, only one of which is obtained by nucleophilic substitution in dimethylformamide. GC-mass spectrometry results support this interpretation. The data indicate that the reaction of aryl thiols with trichloropropene does not exhibit regioselectivity or stereoselectivity. It follows that the intermediate radical can form on either carbon of the trichloropropene double bond. References 9: 6 Russian, 3 Western.
[336-12126]

UDC 540.07.311'824'185

SYNTHESIS OF BINARY PHOSPHATE: $\text{Na}_5\text{Ti}(\text{PO}_4)_3$

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 7, Jul 85
(manuscript received 11 Mar 84) pp 770-771

SLOBODYANIK, N. S., NAGORNIY, P. G. and BYALKOVSKIY, G. D., Kiev State
University imeni T. G. Shevchenko

[Abstract] Studies on a mixture of Na_2O , P_2O_5 and TiO_2 over a temperature range of 650-1150°C resulted in crystallization of $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ at 710-725°C. The binary phosphate consisted of transparent, irregular hexagonal crystals that showed strong light dispersion and weak birefringence ($N_p = 1.673$ and $1.679 < N_g < 1.682$). The structure of the isolated compound was based on elemental analysis and IR spectra. Figures 1; references 8: 7 Russian, 1 Western.
[341-12172]

UDC 541.122

ENTHALPY OF FORMATION OF LIQUID BINARY Si-La (Gd, Dy, Ho, Er) SYSTEMS

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 7, Jul 85
(manuscript received 24 Feb 84) pp 775-777

BATALIN, G. I., SUDAVTSOVA, V. S. and STROGANOVA, N. V., Kiev State
University

[Abstract] Isothermic calorimetry was employed in the determination of the integral and partial enthalpies of mixing of liquid binary melts of Si with La, Gd, Dy, Ho or Er. Determinations of ΔH and ΔH_{re} for different activities of the rare earth elements are tabulated, and they show the former to range from ca. -3 to -26 kJ/mole, and the latter from ca. -120 to -200 kJ/mole. References 2 (Russian).
[341-12172]

NITROGEN COMPOUNDS

UDC 547.796.1'541.49

COMPLEX FORMATION BETWEEN 1- AND 2-ALKYL TETRAZOLES AND Cu(II) CHLORIDE AND RHODANIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 5 Nov 83) pp 516-522

DEGTYARIK, M. M., GAPONIK, P. N., LESNIKOVICH, A. I. and VRUBLEVSKIY, A. I.,
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[Abstract] IR and ESR spectroscopies were used to follow the formation of novel complexes formed between a series of 1- and 2-alkyl tetrazoles and Cu(II) rhodanide or chloride. 1-Alkyl tetrazoles readily yielded crystalline complexes at room temperature in organic solvent (methanol, ethanol, acetone or in binary systems with diethyl ether) with yields approaching 96%. In the case of $\text{Cu}(\text{NCS})_2$, up to 1-2% water was tolerated, and up to 20% water in studies with CuCl_2 . In the case of complexing with 2-alkyl tetrazoles, water concentration had to be limited to 5%. Independent of the reactant ratios and the nature of the electron acceptor and alkyl tetrazole, the complexes had the general formula CuX_2L_2 , where $\text{X} = \text{Cl}$ or NCS and $\text{L} = \text{alkyl tetrazole}$. The alkyl tetrazoles were thus shown to be monodentate ligands; the greater ease with which the 1-alkyl tetrazoles formed complexes served as a basis for the separation of the 1- and 2- isomers. References 14: 1 Czech, 10 Russian, 3 Western.
[331-12172]

SYNTHESIS OF DI- AND TRISUBSTITUTED NITROSOHYDRAZINES FROM N-ALKYL-N-NITROSOHYDRAZINES

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 21, No 6, Jun 85
(manuscript received 4 May 84) pp 1228-1232

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[abstract] N-Propyl-N-nitrosohydrazine was reacted with methyl amine (as the sodium or potassium salt) in liquid ammonia, and then with ethyl, propyl, butyl, chlorobutyl, allyl or propargyl halide to give the N,N'-disubstituted nitrosohydrazine. Similarly, a propyl group was added to N-butyl-N-nitrosohydrazine and a benzyl group to N-benzyl-N-nitrosohydrazine. A third substituent was added to the N-propyl-N'-ethyl or N-butyl-N'-propyl derivatives, ethyl or allyl for the former and methyl for the latter. The fact that monoalkylation was possible is connected with the relative stability of the various anions involved. Equimolar ratios of reagents were optimal for producing N,N'-disubstituted N-nitrosohydrazines. Tetrahydrofuran was also used as a solvent form some of the reactions, in which case potassium salts were more soluble, and thus faster reacting, than sodium. Bromides and iodides were more reactive than chlorides, permitting the synthesis of N-propyl-N'-(4-chlorobutyl)-N-nitrosohydrazine. Under the most favorable conditions yields of 70-90% were achieved. Structures were confirmed by elemental analysis, IR and functional group color tests. References 5: 2 Russian, 3 Western.
[336-12126]

UDC 547.583.1:541.127

STRUCTURE AND REACTIVITY OF HYDRAZINE DERIVATIVES. PART 42. KINETICS OF REACTION OF BENZENESULFONEHYDRAZIDE WITH PHENYLISOCYANATE IN BENZENE WITH ADDED TRANSITION METAL ACETYLACETONATES

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 21, No 6, Jun 85
(manuscript received 8 Dec 83) pp 1242-1249

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[Abstract] The kinetics of the reaction of benzenesulfonehydrazide with phenylisocyanate were studied in the presence of the catalytic acetylacetonates of Cr(III), Fe(III), Co(III), Co(II), Ni(II) and Zn(II) ions. The decreased frequency of the SO₂ group IR band indicated that the sulfone was coordinated to the metal through the oxygen. The IR bands for the acetylacetonate and hydrazine were also shifted. However, the sulfone adducts did not show

greater catalytic activity than the metal acetylacetonates, except for zinc. This indicates that the metal acetylacetonate-isocyanate complex possesses the catalytic activity. Addition of free acetylacetone decreased the reaction rate, indicating that the isocyanate replaces one of the metal ligands. The inhibitory effect of small amounts of pyridine confirmed the role of inner-sphere coordination. A ternary complex is proposed as the second intermediate in the reaction mechanism. The activity of the catalyst depended on the nature of the transition metal. Figures 3; references 18: 12 Russian, 6 Western.
[336-12126]

UDC 547.874.07

SYNTHESIS OF 2-ALKYL-4,6-BIS(TRICHLOROMETHYL)-1,3,5-TRIAZINES CONTAINING LONG-CHAIN ALKYL RADICALS OF NORMAL STRUCTURE

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 21, No 6, Jun 85
(manuscript received 3 May 84) pp 1306-1311

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[Abstract] The cocyclotrimerization of trichloroacetonitrile with pentyl, decyl, undecyl, dodecyl, pentadecyl or heptadecyl nitrile was studied. The highest yield of 2-pentyl-4,6-(trichloromethyl)-1,3,5-triazine, 87%, was achieved with a molar ratio of trichloroacetonitrile to alkyl nitrile of 1.4-1.5 to 1.0. The reaction mixture was saturated with dry HCl at -15 C to -10 C, then heated to 100 C to 110 C. About 10-12% of 2,4,6-tris-(trichloromethyl)-1,3,5-triazine was formed, and could not be eliminated by changing reaction conditions. For the larger alkyl substituents heating to 145 to 155 C for several hours was necessary. Structures were confirmed by IR, PMR and mass spectroscopy. The main mass spectroscopy fragmentation pathway involved elimination of three chlorine atoms. The secondary pathway included beta-decomposition of the alkyl radical with MacLafferty rearrangement. References 13: 8 Russian, 5 Western.
[336-12126]

ORGANOMETALLIC COMPOUNDS

UDC 547.258.11

SOLVENT EFFECTS ON RATE OF REACTION OF ORGANOTIN COMPOUNDS WITH OZONE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 1 Aug 84) pp 483-487

TARUNINA, V. N., TARUNIN, B. I. and ALEKSANDROV, Yu. A.

[Abstract] Kinetic studies were conducted on the reaction of tetrabutyltin, dimethyl-di-tert-butyltin, triethylchlorotin, and dichloro-di-tert-butyltin with ozone in carbon tetrachloride, acetone and the binary solvents acetone/ CCl_4 and acetone/water over a wide range of dielectric constants (2.24-37). At 0 and 5°C, the oxidation reactions followed second order kinetics in all the solvent systems, with the kinetic parameters unaffected by the ozonolytic products. Analysis of reactivity in relation to the dielectric constants demonstrated that reactivity of the organotin compounds was affected by specific and nonspecific solvation. This effect was ascribed to the increased polarity of the organotin compound-ozone complex, as indicated by dipole moment (1.37-1.49) and charge (0.14-0.15) calculations for the activated complex. Figures 1; references 12 (Russian).
[331-12172]

UDC 546.261

EFFECTS OF PRESSURE AND TEMPERATURE ON SYNTHESIS OF TERNARY MNi_8C_2 COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 3 Jul 84) pp 529-534

PUTYATIN, A. A., SEMENENKO, K. N. and NIKOL'SKAYA, I. V., Moscow State University imeni M. V. Lomonosov

[Abstract] Experimental data are presented on the synthesis of a series of novel ternary carbides with the composition of MNi_8C_2 , where M = La, Ce, Pr, Nd or Sm, under pressures covering 10^{-2} to 10^{-5} Pa and 10^9 to 8×10^9 Pa and temperatures of 600-2100°K. The specific composition of MNi_8C_2 was confirmed

by x-ray analysis and metallographic studies, leading to tabulation of structural data on the crystals. Differential thermal analysis demonstrated that the melting point for LaNi_8C_2 was 1390°K , with those for the other isostructural compounds falling quite close. Air-stored MNi_8C_2 compounds were highly resistant to hydrolysis, significantly exceeding the resistance of $\text{M}_2\text{Ni}_5\text{C}_2$ and MNiC_2 compounds. The effects of high pressure in the course of synthesis found manifestation either in enhancing the rate of carbide synthesis or in altering the boundary field phases of MNiC_2 , $\text{M}_2\text{Ni}_5\text{C}_2$ and MNi_8C_2 in going from 10^2 - 10^5 Pa to 1-8 GPa. References 7 (Russian).
[331-12172]

UDC 541.11+547.242

ENTHALPY OF MIXING OF ARSENIC TRICHLORIDE WITH SELECTED HETEROORGANIC COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 11 Jul 84) pp 583-586

ZORIN, A. D., TSVETKOV, V. G., KARATAYEV, Ye. N., FESHCHENKO, I. A.,
PEROV, V. A. and GATILOV, Yu. F.

[Abstract] Calorimetric studies were conducted on the enthalpy of mixing of AsCl_3 with several heteroorganic compounds at 298°K . Measurements with an adiabatic calorimeter on mixtures containing 10 to 90 mole% AsCl_3 demonstrated that with CH_3I a maximum change in enthalpy (-1.76 kJ/mole) was obtained with a 1:1 mixture, with greater or lesser concentrations of AsCl_3 leading to a decrease in enthalpy change. Changes in enthalpy on mixing with AsEt_3 and PbEt_3 were much greater. The maximal change with AsEt_3 (-31.8 kJ/mole) was obtained with a 1:1 mixture, whereas a maximal change in enthalpy with PbEt_3 (-80.3 kJ/mole) was obtained with a 40 mole% AsCl_3 mixture. On reaction with CH_3I , PbEt_3 and AsEt_3 coordinated compounds were formed, with the adduct formed with AsEt_3 disproportionating into elemental As and triethylarsine dichloride. The high heat release on reaction with PbEt_3 was due to formation of mixed ethyl halides. Figures 1; references 10: 7 Russian, 3 Western.
[331-12172]

MASS SPECTROMETRY OF COMPLEXES BETWEEN Co(O), Mo(O), Ni(II) OR Cu(I) AND PHOSPHOROUS ACID AMIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 18 May 84) pp 1274-1283

NIFANT'YEV, E. Ye., BLOKHIN, Yu. I., TELESHEV, A. T., CHIKISHEV, Yu. G.,
ROZYNOV, B. V. and VAKHTBERG, G. A., Moscow State Pedagogic Institute
imeni V. I. Lenin

[Abstract] Mass spectrometric analysis was applied to complexes formed between amidophosphorous acid and cyclic and acyclic amidophosphites and Cu(I), as well as to previously undescribed complexes with Co(O), Mo(O) and Ni(II). The nature of the organophosphorus ligand had a profound effect on the complexes formed with octacarbonyldicobalt. With amidophosphorous acid, mononuclear complexes were formed, while the amidophosphites yielded binuclear coordination compounds. Coordination of the phosphamides on the metal atoms was via the phosphorus atom of the ligand. Decomposition of the complex compound involved initially breakage of the P-N bond. In the case of complexes involving metal halides, the breakdown sequence consisted of a loss of the metal atom as the first step with the formation of a X·L fragment (X = halogen, L = ligand), followed by elimination of the halogen atom. Coordination compounds formed by elimination of the halogen atom. Coordination compounds formed with carbonyls showed a sequence consisting of initial loss of CO and then of the metal. References 12: 3 Russian, 9 Western.
[337-12172]

UDC 547.257.6.07

SYNTHESIS OF BENZENETRICARBONYLCHROMIUM, -MOLYBDENUM AND -TUNGSTEN

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 21 Aug 84) pp 1323-1327

MAGOMEDOV, G. K. -I., FRENKEL', A. S. and BLOKHINA, Ye. I.

[Abstract] A process was devised for the continuous synthesis of benzene-tricarbonylchromium (I), -molybdenum (II) and -tungsten (III) with removal of carbon monoxide at 160-170°C for I and II, and at 180-200°C for III. The basic approach consisted of the replacement of 3 molecules of CO in the respective hexacarbonyls (Cr(CO)₆, Mo(CO)₆ or W(CO)₆) by a benzene molecule. Using catalytic concentrations of pyridine or derivatized pyridine (Py_nM(CO)_{6-n}) raised the yields of I to 95% and of II to 71%. The synthesis of III required the addition of NH₄BF₄ for yields in the range of 81%. References 13: 4 Russian, 9 Western.
[337-12172]

CARBAMYLDICYANOMETHANIDE AND CARBAMYL CYANAMIDE COMPLEXES OF 3d-METALS
CONTAINING PHOSPHINOXIDE LIGANDS

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 7, Jul 85
(manuscript received 6 Apr 84) pp 679-683

LAMPEKA, R. D., SKOPENKO, V. V. and ZAPOROZHETS, N. V., Kiev State
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[Abstract] Description is provided of the synthesis of carbamyldicyanomethanide and carbamylcyanamide coordination compounds of selected 3d-metals (Co(II), Ni(II), Cu(II), Zn(II)), containing phosphin oxide ligands (hexamethylphosphotriamide or triphenylphosphin oxide). IR and EPR spectroscopic analysis of these previously-undescribed complexes demonstrated that the carbamyldicyanomethanide compounds were organized into a pseudooctahedral conformation, with the ligand coordinated with the metal through the nitrogen of the nitrile group and the oxygen of the carbamyl group. The acid ligand in this case performed a bridge function. The spectroscopic information for the carbamylcyanamides was consonant with a tetrahedral structure around the central atom, with the anion having a monodentate function. Figures 3; references 6: 4 Russian, 2 Western.
[341-12172]

STRUCTURE AND THERMAL CHARACTERISTICS OF GASEOUS Ni(II)BIS-2,4-IMINOPENTANATE

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 7, Jul 85
(manuscript received 23 Mar 84) pp 683-685

MAZURENKO, Ye. A., ZHELEZNOVA, L. I., KIN', T. V. and POSIL'SKIY, O. A.,
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Sciences, Kiev

[Abstract] Derivatographic studies on Ni(II)bis-2,4-iminopentamate in the gaseous state demonstrated that the compound sublimes at 90°C and retains structural stability over the 90-300°C interval. Dissociation begins at ca. 300°C and is completed at 345°C. Analysis of EPR and IR spectra obtained for gaseous Ni(II)bis-2,4-iminopentamate indicated that the compound retains the square planar structure characteristic of the solid state in solution. Figures 3; references 7: 3 Russian, 4 Western.
[341-12172]

UDC 547.241:543.422.25

THERMAL DECOMPOSITION OF NITRILOTRIMETHYL PHOSPHONIC ACID IN AQUEOUS SOLUTIONS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 27 Feb 84) pp 534-538

KASLINA, N. A., POLYAKOVA, I. A., KESSENIKH, A. V., ZHADANOV, B. V.,
RUDOMINO, M. V., CHURILINA, N. V. and KABACHNIK, M. I., All-Union
Scientific Research Institute of Chemical Reagents and Especially
Pure Chemicals, Moscow

[Abstract] The use of nitrilotrimethyl phosphonic acid in various chemical processes at high temperatures led to a study on its decomposition under such conditions in aqueous solutions. The NMR and PMR studies on the products were carried out after thermal decomposition of the 1 M acid at pH 1-11 and in 5 M HCl at temperatures ranging from 100 to 250°C. Studies with molybdenum glass sealed ampules demonstrated that decomposition commences in the aqueous solutions at pH 1.5, and in the 5 M HCl at 125°C. At 160°C, the decomposition products exceed the acid ten-fold. On the basis of the spectral data, it became evident that at pH 1.5 or greater nitrilotrimethyl phosphonic acid decomposes via breakage of the C-P bonds, and in 5 M HCl as a result of N-C bond rupture. Figures 2; references 3: 2 Russian, 1 Western.
[331-12172]

UDC 546.18

REACTION OF DIIMIDOPHOSPHENIC (I) AND IMIDOTHIOPHOSPHENIC (II) ACID AMIDES ($\sigma^{3\lambda^5}$ -PHOSPHORUSAZAYLIDS) WITH ORGANOLITHIUM COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 24 Apr 84) pp 538-543

ROMANENKO, V. D., SHUL'GIN, V. F., SKOPENKO, V. V. and MARKOVSKIY, L. N.,
Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] The feasibility of C-phosphorylation with $\sigma^{3\lambda^5}$ -phosphorusazaylids of organolithium compounds was studied with I and II, using methyllithium and

phenyllithium as the target compounds. In view of the highly nucleophilic nature of the organolithium compounds, the reactions proceeded energetically at -78°C in equimolar mixtures. In both cases, C-phosphorylation led to the synthesis of P(V)-C bonds and derivatized phosphonic acids. In the reaction of I with methyllithium, the N,N,N',N''-tetrakis(trimethylsilyl)-amide reacted with aluminum trichloride and titanium and tin tetrachlorides to form chelate complexes with the metals. II reacted in an analogous manner with the organolithium compounds to yield diamides of thiophosphonic acid. The approaches taken here represent a novel pathways to the synthesis of compounds with the P(V)-C bond, which are potentially useful in coordination chemistry. References 10: 2 Russian, 8 Western.
[331-12172]

UDC 547.241

REACTION OF TETRAALKYLMETHYLENEBISPHOSPHONITES WITH AROMATIC ALDEHYDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 17 Apr 84) pp 553-559

ODINETS, I. L., NOVIKOVA, Z. S. and LUTSENKO, I. F., Moscow State University imeni M. V. Lomonosov

[Abstract] The reaction of tetraethyl- and tetraisopropylmethylenebisphosphonites with a series of aromatic aldehydes (benzaldehyde, p-chlorobenzaldehyde, p-methoxybenzaldehyde, furfural) in 1:1 ratio at $120-130^{\circ}\text{C}$ for 12-15 h resulted in oxidation of the phosphonite groups and formation of corresponding P(V)-substituted phosphonites and methylenebisphosphonates. In terms of yields, the former products predominate, with the latter accounting for 10-20% of the conversion and alpha-alkoxybenzylphosphinate accounting for only 5% of the yield in reactions with benzaldehyde and p-methoxybenzaldehyde. Reactions with o- and p-nitrobenzaldehydes yielded the corresponding methylenebis(1,3,2-dioxaphosphoranes). In addition to the oxidation of the methylenebisphosphonites, diarylethylenes were also isolated and represented reductive dimerization of the aldehydes. References 14: 5 Russian, 9 Western.
[331-12172]

THIOACETIMIDOYLPHOSPHITES: SYNTHESIS AND REACTION WITH PROTIC REAGENTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 8 Feb 84) pp 559-562

AL'FONSOV, V. A., PUDOVNIK, D. A., BATYYEVA, E. S. and PUDOVNIK, A. N.,
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[Abstract] Details are provided on S-phosphorylation of thioacetamide by dialkylchlorophosphites, yielding dialkylthioacetimidoylphosphites. The latter decompose on distillation into dialkylthiophosphites and acetonitrile due to the presence of a mobile proton on the nitrogen atom which migrates to the phosphorus atom. Subsequent redistribution of electron density in the molecule results in a splitting off of the acetonitrile. Reaction of the dialkylthioacetimidoylphosphites with aliphatic amines and alcohols as well as HCl leads to thioimidoyl group substitution with formation of thioacetamide and the corresponding P(III) derivative. Evidently, the thioacetimidoyl on the P atom behaves as a pseudohalide in reaction with protic reagents. References 5: 3 Russian, 2 Western.
[331-12172]

UDC 547.26+661.718.1

PHOSPHORUS-CONTAINING PODANDS: DI- AND TRIPODANDS WITH PHOSPHINYLMETHYL END GROUPS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 23 Jul 84) pp 562-566

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[Abstract] Previously, a description was provided of the synthesis of monopodands, representing more accessible analogs of crown ethers [Tsvetkov, Ye. N., et al., Zh. Organicheskoy Khimii, 54: 2338, 1984]. In order to improve the efficiency of the acyclic analogs in complexing with alkali metal cations, phosphorus-containing di- and tri-podands were synthesized by reacting halogenated methylphosphine oxides with derivatized pyrocatechol or hydroxymethylphosphine oxides. The resultant products had the general formula $R_mP(O)[CH_2(OA)_nOCH_2P(O)R_2']_{3-m}$, where $n = 0$ or 1 and $m = 0$ or 1 , and

OA = ethylene glycol or pyrocatechol fragment. PMR and NMR spectroscopic data confirmed synthesis of compounds with two or three phosphinylmethyl end groups. References 7: 4 Russian, 3 Western.
[331-12172]

QUINO(4)CYANINES WITH PHOSPHORUS SUBSTITUENTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 15 May 84) pp 566-571

TOLMACHEV, A. A., KOZLOV, E. S., KACHKOVSKIY, A. D. and SLOMINSKIY, Yu. L.,
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[Abstract] A series of symmetric and asymmetric quino(4)cyanine dyes with phosphorus-containing substituents were synthesized by the reaction of lepidine salts with ethyl orthoformate, or malonic or glutaric dianilide hydrochlorides to yield, respectively, the carbo-, dicarbo- or tricarbo-cyanine dyes. The presence of a phosphorus substituent in the heterocyclic nuclei intensified absorption in a manner analogous to that seen with carbonyl substituents, with the auxochromic effects diminished in relation to the length of the polymethine chain. The largest auxochromic effect was seen with substituents with a phenyl group on the phosphorus atom, with the effects diminished by the presence of ethyl groups and even more so with amide groups. The phosphorus substituents exerted similar hypsochromic effects to those seen with carbonyl substituents, indicating similar solvation effects with both classes of substituents. References 14: 13 Russian, 1 Western.
[331-12172]

UDC 541.62:547.241

INTERPRETATION OF PHOTOELECTRON SPECTRA OF DIMETHYLPHENYLPHOSPHINE BY CNDO/2 CALCULATIONS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 23 Dec 83) pp 571-576

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Coal Chemical Synthesis, Irkutsk State University imeni A. A. Zhdanov

[Abstract] CNDO/2 calculations were conducted on the photoelectron spectra of dimethylphenylphosphine and phenylphosphine to resolve the question of p- π orbital interaction. Analysis of the data for the A and B rotamers of both compounds, and comparison with similar calculations for aniline and dimethylaniline, on the three upper-occupied molecular orbitals, showed marked p- π interaction. The controversy has in general stemmed from the overlap of the experimental spectra of the A and B rotamers. Optimal conditions for such studies require an A:B ratio of conformers for dimethylphosphine to be 0.5:0.5, and for methylphosphine 0.66:0.33. References 7: 4 Russian, 3 Western.
[331-12172]

NMR SPECTROSCOPY OF VINYLIDENEDIPHOSPHONIC ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 2 Feb 84) pp 579-582

BERDNIKOV, Ye. A., LEVIN, Ya. A., GAZIZOVA, L. Kh. and CHERNOV, P. P.,
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Branch, USSR Academy of Sciences; Kazan State University
imeni V. I. Ul'yanov-Lenin

[Abstract] ^1H , ^{13}C and ^{31}P NMR spectroscopies were conducted on vinylidene-diphosphonic acid (I) formed by dehydration of hydroxyethylidenediphosphonic acid to determine whether the phosphoryl group in I migrates with formation of E- or Z-isomers. The data showed that no migration occurs and that such isomers are not formed as a result of high temperature (200°C) treatment. PMR studies on complete ionization of I into a tetra-anion indicated that the electron density on C^2 increases and serves to shield the olefin protons. Consequently, there is a decrease in the sum of the $[\text{}^3\text{J}_{\text{PH}}^{\text{trans}} + \text{}^3\text{J}_{\text{PH}}^{\text{cis}}]$ con-

stants and an increase in the value of Δ_{v} . Figures 2; references 14:
6 Russian, 8 Western.
[331-12172]

EFFECTS OF SUBSTITUENTS ON PHOSPHORUS ATOM ON EFFECTIVE PARTITION CONSTANTS OF DITHIOPHOSPHORIC ACIDS IN WATER-ORGANIC SOLVENT SYSTEMS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 2 Feb 84) pp 677-680

TOROPOVA, V. F., GARIFZYANOV, A. R., PANFILOVA, I. Ye., SAVEL'YEVA, N. I.
and CHERKASOV, R. A., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] Potentiometric titration was employed in the determination of effective partition constants of a series of O,O-dialkyldithiophosphoric acids in binary water-organic solvent systems in relation to substituents on the phosphorus atom. The experimental data demonstrated that the partition constants increase in relation to the size and degree of branching of the alkoxy groups. On the basis of these observations a biparametric correlation equation is proposed for a quantitative assessment of substituent effect on the partition constant, $\lg K' = a + \delta \sum E_s' + \gamma \sum \pi$, where E_s' is the steric constant of the substituent, π is the hydrophobic constant of the substituent, δ is the correlation constant describing susceptibility of the series to substituent steric effects, γ is the correlation constant describing susceptibility to substituent hydrophobic effects, and a is a constant. References 8:
4 Russian, 4 Western.
[331-12172]

UDC 541.49+546.661.718.1+547.333.4+519.24.27

COMPLEX COMPOUND FORMATION BETWEEN MAGNESIUM AND ALKALINE EARTH METALS WITH
2-HYDROXYPROPYLENE-1,3-DIAMINO-N,N,N',N'-TETRAMETHYLENEPHOSPHONIC ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 30 Jul 84) pp 680-685

SAMAKAYEV, R. Kh., NIKOLAYEVA, L. S., MATKOVSKAYA, T. A., YEVSEYEV, A. M.
and DYATLOVA, N. M., All-Union Scientific Research Institute of Chemical
Reagents and Especially Pure Chemicals, Moscow; Moscow State University
Imeni M. V. Lomonosov

[Abstract] 1,3-Diamino-N,N,N',N'-tetramethylenephosphonic acid (I),
synthesized by the reaction of 1,3-diaminopropan-2-ol with formaldehyde and
 PCl_3 , was tested for its effectiveness in complex formation with magnesium and
alkaline earth metals in relation to concentration and pH. Potentiometric
studies led to accurate determination of stability constants for complexes of
different compositions. The presence of inflection points on the high fre-
quency titration plots at the metal:ligand ratios of 1:1 and 2:1 indicated the
existence of two types of complex compounds represented by ML and M_2L .
Tabulated data are presented on the logs of the stability constants for the
complexes M_2L and MH_iL , with $i = 0, 1, 2, 3, 4$ or 5, showing an increase in
the value of the constants with an increase in the value of i . Figures 2;
references 11: 9 Russian, 2 Western.
[331-12172]

UDC 547.341

REACTION OF S,S-DIETHYLPHENYLDITHIOPHOSPHONITE WITH NITRILIMINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 13 Jun 84) pp 695-696

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[Abstract] S,S-Diethylphenyldithiophosphonite was found to react at room
temperature with C-benzoyl- and ethoxycarbonyl-N-arylnitrilimines under
argon to yield unstable azomethylenephosphoranes. On hydrolysis, the latter
lost ethyl mercaptan to give thiophosphinates. The structure of the products
was confirmed by IR, MPR and NMR spectroscopies. References 1 (Russian).
[331-12172]

REACTION OF GLYCOLPHOSPHOROUS ACID N,N-DIALKYLAMIDES WITH OXIMES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 30 May 84) pp 697-698

OSIPOVA, M. P., VOLKOVA, R. V. and ZLOBINA, I. A., Chuvash State University
imeni I. N. Ul'yanov, Cheboksary

[Abstract] Ethyleneglycolphosphite N,N-diethylamide reacts at room temperature with benzophenone and acetaldehyde oximes to yield an alkylideneamidophosphate and diethylamine. The amidophosphate apparently involves an unstable intermediate P(III) compound which isomerizes into the amidophosphate. Reaction of ethyleneglycolphosphite with benzoquinone oxime in the presence of triethylamine also yields an amidophosphate. With acetaldoxime ethylideneamidophosphate is formed, which on heating is converted into ethyleneglycolphosphite with release of acetonitrile. References 1 (Western).
[331-12172]

1,3-DIAZA-2 λ^4 ,4 λ^4 -DIPHOSPHETIDINE-2,4-DIONIUM DIHALIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 28 Jun 84) pp 700-701

KOVENYA, V. A., MARCHENKO, A. P. and PINCHUK, A. M., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Tris(N,N-dimethylamido)halophosphonium halides releases methyl halides at 235-240°C under vacuum (10^{-5} mmHg) and yield compounds with a short lifetime that are presumably diamidochloro-(bromo)-phosphazomethanes(I). The latter undergo rapid conversion to 1,3-diaza-2 λ^4 ,4 λ^4 -diphosphetidine-2,4-dionium dihalides, representing phosphazo dimers with two phosphonium groups. The compounds I are crystalline substances subject to hydrolysis by moisture in the air, weakly soluble in nitromethane and insoluble in most organic solvents. References 4: 3 Russian, 1 Western.
[331-12172]

SYNTHESIS OF ALKYL CYCLOALKENYL SULFIDES FROM ALPHA-ALKYLTHIOCYCLOALKYLDICHLOROPHOSPHONATES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 13 Apr 84) pp 703-704

AL'FONSOV, V. A., NIZAMOV, I. S., BATYYEVA, E. S. and PUDOVNIK, A. N.,
Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov,
Kazan Branch, USSR Academy of Sciences

[Abstract] A novel approach has been devised for the production of vinyl sulfides, consisting of heating alpha-alkylthiocycloalkyldichlorophosphonates at 100-150°C in a vacuum distillation apparatus at 6×10^{-3} mmHg. The process yielded alkylcycloalkenyl sulfides in ca. 75% yields, the structure of which was confirmed spectroscopically. References 4 (Western).
[331-12172]

REACTION OF DIETHYLDITHIOCHLOROPHOSPHITE WITH SILYL PHOSPHITES AND DIETHYL PHOSPHITE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 3, Mar 85
(manuscript received 9 Jul 84) pp 704-705

AL'FONSOV, V. A., ZAMALETDINOVA, G. U., BATYYEVA, E. S. and PUDOVNIK, A. N.,
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[Abstract] Diethyldithiochlorophosphite was found to react with diethyltrimethylsilyl phosphite and tris(trimethylsilyl)phosphite with the formation of 1,1-diethyldithiophosphine-2-oxides. Specific conditions are described for the synthesis of 1,1-diethyldithio-2,2-diethoxydiphosphine-2-oxide and 1,1-diethyldithio-2,2-bis(trimethylsiloxy)diphosphine-2-oxide, structures of which were confirmed spectroscopically. In terms of its stabilizing effect, the alkylthio group on the P(III) atom behaved more like an alkyl group than an alkoxy group. References 4 (Russian).
[331-12172]

TERNARY THIOPHOSPHORYL-MERCAPTOYLID TAUTOMERISM. PART 2. SYNTHESIS AND STRUCTURE OF [(DIPHENYLTHIOPHOSPHORYL)BENZOYLMETHYL]TRIPHENYLPHOSPHONIUM SALTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 25 Jun 84) pp 1234-1244

ALADZHEVA, I. M., PETROVSKIY, P. V., KLEMENKOVA, Z. S., LOKSHIN, B. V., MASTRYUKOVA, T. A. and KABACHNIK, M. A., Institute of Heteoorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] As part of a study of ternary thiophosphoryl-mercaptoylid tautomerism, a spectroscopic analysis was conducted on the structure of [(diphenylthiophosphoryl)benzoylmethylene]triphenylphosphorane (I). I was synthesized by the reaction of [(diphenylphosphino)benzoylmethylene]triphenylphosphorane with powdery sulfur in CH_3CN at 50°C , and recrystallized from alcohol. Protonation of I resulted in a tautomeric mixture of CH and OH phosphonium salts. In ethanol and methanol bromide the salts are virtually completely enolized, while in CHCl_2 and CH_2Cl_2 the CH form predominates. In a CHCl_3 - $\text{C}_2\text{H}_5\text{OH}$ solvent mixture (8:1) approximately equivalent concentrations of both forms are present. Methylation of I consisted of two pathways: O-methylation of the oxygen of the carbonyl group, and the product of S-methylation undergoing an intramolecular Wittig rearrangement. Figures 2; references 15: 10 Russian, 5 Western. [337-12172]

REACTIVITY OF CYCLIC AND ACYCLIC HYDROPHOSPHORYL COMPOUNDS IN ELECTROPHILIC ADDITIONS TO ACETALKETENES AND ENAMINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 4 Jun 84) pp 1244-1253

OVCHINNIKOV, V. V., CHEREZOV, S. V., CHERKASOV, R. A. and PUDOVNIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] Studies were conducted on the reactivity of 5-, 6- and 7-membered cyclophosphorous acids with acetalketenes and enamines to assess their efficiency in electrophilic addition reactions in relation to efficiency as H donors. The 5-membered 2,3-butylene-1,2-propylene- and pinacone phosphites react exothermically with diethylketene acetal at room temperature. The 6-membered neopentylene- and salicyl-, and the 7-membered o-bisphenylene--as well as the acyclic diphenyl- and di-beta-chloroethyl phosphorous acids--also reacted with diethylketene acetal in the absence of a catalyst, requiring, however, 60 - 80°C for 2-4 h. The additions followed Markownikow's rule in all cases. The reactions were accompanied by the appearance of a bright

yellow or orange color, characteristic of the formation of donor-acceptor complexes. Only 2,3-butylene- and pyrocatechol phosphites reached with diethylthioketene acetal, apparently because the double bond in the latter is less nucleophilic than in diethylketene acetal. Noncatalytic reaction was also seen with 1-morpholino-2-methyl-1-propene in the case of 2,3-butylene-phosphorous acid at room temperature, and at 50-60°C with pinacone-, neopentylene- and salicyl phosphites. Acyclic dialkyl phosphites required even higher temperatures (80-100°C). Therefore, these studies demonstrated a direct correlation between H donor efficiency of phosphorous acids and their involvement in electrophilic additions. Figures 2; references 32:

21 Russian, 11 Western.

[337-12172]

UDC 547.1'118

REACTION OF DIETHYLDITHIOCHLOROPHOSPHITE WITH ALPHA, BETA-UNSATURATED ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 5 Jun 84) pp 1253-1257

AL'FONSOV, V. A., NIZAMOV, I. S., BATYYEVA, E. S. and PUDOVNIK, A. N.,
Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov,
Kazan Branch, USSR Academy of Sciences

[Abstract] Diethyldithiochlorophosphite reacted with acrylic and methacrylic acids in sealed ampules at room temperature for 28 h to yield the corresponding diethyl-beta-(chloroformyl)alkylthiophosphonates (I). The I products were unstable on storage and underwent gradual conversion to S-ethyl-beta-(ethylthiocarbonyl)alkylchlorothiophosphonates. On reaction with methanol and ethylmercaptan, I yielded the corresponding derivatized diethyldithiophosphonates. References 12: 8 Russian, 4 Western.
[337-12172]

UDC 547.752'26.118.07

INDOLE PHOSPHORYLATION BY P(III) ACID CHLORIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 21 Dec 83) pp 1257-1262

GUREVICH, P. A., RAZUMOV, A. I., KOMINA, T. V., KLIMENTOVA, G. Yu. and ZYKOVA, T. V., Kazan Institute of Chemical Technology imeni S. M. Kirov

[Abstract] IR, NMR and PMR spectroscopic data are presented on the phosphorylation of indole by P(III) acid chlorides, to expand the data base available for such reactions with mono- and dichloroamidophosphites, mono- and dichlorophosphites, and mono- and dichlorophosphines. The monochloroamidophosphites and the monochlorophosphines served as N-phosphorylating

agents. The monochlorophosphites served to phosphorylate both the N and the C³ atoms of indole. Reaction of indole with P(III) acid dichlorides led to the formation of phosphorylated bisindolephosphites, -phosphonites and -phosphinites. References 5 (Russian).
[337-12172]

UDC 546.561+547.241+542.42

COMPLEXES OF Cu(I) HALIDES AND PHOSPHOROUS ACID AMIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 13 Apr 84) pp 1265-1273

NIFANT'YEV, E. Ye., TELESHEV, A. T., BLOKHIN, Yu. I., ANTIPIN, M. Yu. and STRUCHKOV, Yu. T.; Moscow State Pedagogic Institute imeni V. I. Lenin

[Abstract] Extensive chemical and spectroscopic studies were conducted on the formation of complexes between various Cu(I) halides and phosphorous acid amide and cyclic and acyclic amidophosphites. The complexes were formed readily in benzene at 20°C with the general formula $Cu_4X_4L_4$ (X = halogen, L = ligand). Greatest stability in air was shown by the iodide complexes and the least was exhibited by the chloride complexes. The complexes were obtained in better than 80% yield and were soluble in most organic solvents. In the complexes, Cu is coordinated with the P atom, with the ³¹P NMR data indicating that the coordination shift of the ligand is directly related to the electronegativity of the halogen and of the heteroatomic substituents on the P atom. Finally, the complexes were found to function as effective phosphorylating agents in the case of ethanol, 2,2-dimethyl-1,3-propylene glycol, and 1,3-butylene glycol. Figures 2; references 19: 10 Russian, 9 Western.
[337-12172]

UDC 547.241+547.73

REACTION OF P(III) ACID ESTERS WITH 2,5-DIBROMOTHIOPHENE CATALYZED BY NiCl₂

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 9 Feb 84) pp 1283-1287

KRASIL'NIKOVA, Ye. A., NEVZOROVA, O. L. (deceased) and SENTEMOV, V. V., Agricultural Institute, Ustinov

[Abstract] Esters of P(III) acids reacted with 2,5-dibromothiophene in the presence of NiCl₂ catalyst to form poorly-soluble diphosphorylated thiophene derivatives via the Arbuzov reaction. To ascertain the role of NiCl₂, UV spectrophotometry and NMR spectroscopy were utilized to monitor a model system consisting of triisopropyl phosphite with the halogenated thiophene.

Addition of the triisopropyl phosphite to a suspension of the dibromothiophene and NiCl_2 led to the appearance of a red complex with maximum absorption at 400 nm, which is typical of Ni(II) complexes with the general composition $[\text{NiL}_2\text{X}_2]$, where L = trialkyl phosphite and X = halide or pseudohalide ions. In the absence of aryl halides, the complex compound retains its stability and configuration for long periods of time, and is unaffected by boiling in benzene. Elevation of the temperature of the triisopropyl-bromothiophene- NiCl_2 system to 150-160°C resulted in the release of gaseous products and change to a pale-blue color. The latter complex had a broad absorption band at 610 nm which is typical of octa- and tetrahedral Ni complexes, and appears to represent internal capture of two molecules of bromothiophene. Its rapid decomposition leads to the appearance of Arbuzov products. References 13: 9 Russian, 4 Western.
[337-12172]

UDC 541.6:547.558.1

HOMOLYSIS OF ORGANOPHOSPHORUS COMPOUNDS. PART 10. SYNTHESIS, STABILITY AND HOMOLYSIS OF ARYLAZO AND ARYLAZOALKYL PHOSPHONATES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 13 Apr 84) pp 1290-1297

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[Abstract] Studies were conducted on the tendency of type A and B azo compounds ($\text{A} = \text{ArN} = \text{NP(O)(OR)}_2$; $\text{B} = \text{C}_6\text{H}_5\text{N} = \text{NCMe}_2\text{P(O)(OC}_6\text{H}_5)_2$) to undergo homolysis, and thereby to serve as a source of free radicals, i.e., phosphonyl radical. Type A compounds purified by silica gel chromatography were found to be stable for several months at low temperatures. This fact excluded them from consideration as a source of free radicals, but suggested their utility as antibacterial and antifungal agents. However, type B compounds--alpha-aryldiazoalkyl phosphonates--underwent homolysis as a result of UV-irradiation. The polarization and composition of the products indicated that in this case homolysis was accompanied by nitrogen release without involvement of the phosphonyl radical. The greater stability of type A compounds (aryldiazo phosphonates) is apparently due to interaction between the azo group and the orbitals of the P atom. Figures 1; references 26: 14 Russian, 12 Western.
[337-12172]

SYNTHESIS OF MONOARYLOXYPENTACHLOROCYCLOTRIPHOSPHAZENES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 25 Oct 84) pp 1297-1302

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Scientific Research Institute of Film Materials and Synthetic Skin, Moscow

[Abstract] An analysis was conducted on the factors determining the efficiency of synthesis of monoaryloxypentachlorocyclotriposphazenes (I) from the reaction of hexachlorocyclotriposphazene (II) with sodium phenolate, p-bromophenolate or p-tert-butyl phenolate. With the use of the phenolates as the nucleophilic reagents in the substitution reactions the optimal ratio of the sodium arylates to II was determined to be 2:1. This decision was in part predicated on the fact that elimination of II from the reaction mixture was an easier process than the isolation of I from among the substitution products. The yield of the monosubstituted products was generally in the 80-100% range at 20°C, and 60-90% at 66°C, in dioxane. With the appropriate phenolate, temperature and length of reaction the system produced highly selective monosubstituted products. Figures 1; references 6: 3 Russian, 3 Western.

[337-12172]

PHOSPHORYLATION OF INDOLE-3-THIOLE BY P(III) ACID CHLORIDES AND AMIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 21 Dec 83) pp 1327-1331

GUREVICH, P. A., RAZUMOV, A. I., KOMINA, T. V., KLIMENTOVA, G. Yu. and
ZYKOVA, T. V., Kazan Institute of Chemical Technology imeni S. M. Kirov

[Abstract] Experimental data are presented on the phosphorylation of indole-3-thiol by P(III) acid amides and chlorides. The reaction with the indole-3-thiol involves both the S-H and the N-H bonds, with the ratio of the products of the S and N phosphorylation dependent on the temperature of the reaction. At -15 to -5°C the yield of S phosphorylated products is 75-85%, a figure which drops to 60% as the temperature is raised to 5 to 15°C. Calculation of the energies of activation for S and N phosphorylation demonstrated that in the former case the value was ca. 33 kJ/mole higher. More stable analogs of the S and N phosphorylated products were obtained by oxidation with elemental sulfur. Oxidation of 1-(phosphoryl)-3-thiol-indoles led to N phosphorylated bis(3-indolyl)disulfides. References 8: 6 Russian, 2 Western.

[337-12172]

SYNTHESIS AND CHARACTERISTICS OF HIGHER-RADICAL ALKYL MAGNESIUM ALUMINUM COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 23 Aug 84) pp 1341-1345

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[Abstract] A relatively simple approach was devised for the synthesis of alkylmagnesiumaluminum compounds, which does not require preactivation of the metals. The reactions were carried out at 80-110°C under dry argon with dropwise addition of the selected alkyl iodide to limit the exothermic effect to the desired temperature range. Alkyl bromides were unsuitable, since they decompose at 100-130°C. The experimental conditions were easily manipulated to produce compounds with the following general formula: $Mg_m Al_n R_{2m+3n}$, where R ranged from C_4H_9 to $C_{10}H_{21}$, and n and m from 0.5 to 30. Cryoscopic data indicated that compounds in which n and $m > 1$ dissociate in benzene, i.e., greatest stability was exhibited by compounds with equimolar composition ($MgAlR_5$). These compounds, useful as catalysts for alpha-olefin polymerization, were stable for several years under argon or nitrogen with full retention of catalytic activity. Figures 1; references 8: 5 Russian, 3 Western.
[337-12172]

UDC 547.241+541.241+543.257+541.67

 ^{31}P -NMR STUDY OF ACID-BASE CHARACTERISTICS OF NEUTRAL ORGANOPHOSPHORUS COMPOUNDS IN ORGANIC SOLVENTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 24 Sep 84) pp 1421-1427

YAKSHIN, V. V., MESHCHERYAKOV, N. M., IGNATOV, M. Ye., LASKORIN, B. N., YAGODIN, V. G. and IL'IN, Ye. G., All-Union Scientific Research Institute of Chemical Technology of the State Committee on the Use of Atomic Energy, Moscow

[Abstract] A ^{31}P -NMR method was developed for the study of acid-base characteristics of neutral organophosphorus compounds falling into the R_3PO category, where $R = C_4H_9$ to C_8H_{17} and C_4H_9O to $C_8H_{17}O$. The studies were conducted with biphasic organic solvent-sulfuric acid (0-12 M) systems and led to the tabulation of acid dissociation constants (pK_{BH^+}) on the basis of $\delta^{31}P$, which were satisfactorily described by the Hammett acidity function. Tabulated data are also provided for experimentally determined correlation coefficients ($r = 0.95-0.99$) between pK_{BH^+} and the sum constant

of the substituents on the P atom ($\Sigma\sigma^{\phi}$), the acid dissociation constants in nitromethane, and the enthalpies of coordinated compound formation with phenol, water, and iodide. In nonpolar solvents basicity was found to rank as follows: phosphinioxides > phosphinates > phosphonates > phosphates. In the case of trihexylphosphin oxide the basicity increased as follows with the different solvents: dodecane < benzene < toluene < 1,1,2,2-tetrachloroethane. Figures 5; references 14: 8 Russian, 6 Western.
[337-12172]

UDC 547.454+547.26.118

SELECTIVE OXIDATION OF HYDROCARBON ALPHA-HYDROXYPHOSPHONATES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 23 Jul 84) pp 1435-1437

GLEBOVA, Z. I., UZLOVA, L. A. and ZHDANOV, Yu. A., Scientific Research Institute of Physical and Organic Chemistry, Rostov State University imeni M. A. Suslov

[Abstract] A novel approach was taken to the preparation of esters of alpha-ketophosphonic acids, bypassing the conventional method involving acylation of derivatized phosphorous acids. The present approach utilized dimethylsulfoxide and acetic anhydride as the activating electrophilic agent for selective oxidation of a hydrocarbon-derivatized alpha-hydroxyphosphonate. A mixture of three corresponding products was obtained, consisting of diethyl 1-O-acetyl-2,4;3,5-di-O-ethylidene-L-threo-cis-(trans-)pent-1-enyl-1 phosphonate, diethyl 1-R,S-1-O-acetyl-2,4;3,5-di-O-ethylidene-L-xylopentahydroxypentyl phosphonate, and diethyl 1-hydroximino-2,4;3,5-di-O-ethylidene-L-xylo-tetrahydroxypentyl phosphonate. References 5: 2 Russian, 3 Western.
[337-12172]

UDC 547.18

P-DI(TERT-BUTYL)PHOSPHINO-C,C-BIS(DIALKYLAMINO)METHYLENEPHOSPHINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 6, Jun 85
(manuscript received 25 Jul 84) pp 1437-1438

ROMANENKO, V. D., SARINA, T. V., POVOLOTSKIY, M. I. and MARKOVSKIY, L. V., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] P-trimethylsilyl-C,C-bis(dialkylamino)methylenephosphines react with di(tert-butyl)chlorophosphine at 20°C in ether to form P-phosphinomethylenephosphines (I) in high yields after 3 h. The I compounds are yellow-orange liquids or low m.p. crystals that react with oxygen to form

a mixture of compounds that are difficult to resolve. However, the I compounds react with sulfur in equimolar mixtures to give P-phosphinothioyl-methylenephosphines (II). A unique feature of I and II compounds is the strong polar absorption on ^{31}P NMR spectra of the P(II) nuclei, due to the strong electron donor effects of the dialkylamino group. References 2:
1 Russian, 1 Western.
[337-12172]

UDC 621.315.615.2

OBTAINING LOW POUR POINT TRANSFORMER OIL

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 3, Mar 85
pp 15-16

KULIYEV, R. Sh., AGAYEVA, R. A., KULIYEV, F. A. and SHAKHBAZOVA, A. I.

[Abstract] The necessity of operating electrical equipment under severe climatic conditions requires transformer oils having lower pour points and viscosities than normally required elsewhere. It was previously shown that such oils may be obtained from a paraffin-base crude from the Sangachaly-Sea oil field by acid-base, contact and adsorption refining. In the present work, it is shown that the same grade oil may also be obtained by blending the Sangachaly-Sea crude with that of Neftyanne Kamni crude in 1:1 ratio. The distillates are first treated with 150% furfural, dewaxed with urea and then further refined with 3% sulfuric acid and 5% Gumbrin bleaching clay. Reference 1 (Russian).
[308-12765]

UDC 665.753.2+665.7.035.6

EVALUATING STRUCTURAL CHANGES IN JET FUELS BY ELECTRICAL CONDUCTIVITY AND VISCOSITY

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 3, Mar 85
pp 20-21

BELOUSOV, A. I. and BUSHUYEVA, Ye. M., All-Union Scientific Research Institute of Petroleum Products

[Abstract] Using the temperature-electrical conductivity relationship of jet fuels alone as an indication of structural changes gives contradictory results. A study was made of using both conductivity and viscosity relationships to temperature at -60° to +80°C. RT, TS-1 and T-1 jet fuels exhibit linear temperature-conductivity curves, indicating no structural changes. A break in the curve below 20°C for T-6 fuels indicates a change. Temperature-viscosity at -50° to +80°C for RT, TS-1 and T-1 fuels are also linear (no

structural change) and confirm the conductivity results. Breaks in these curves at -40° and at $+20^{\circ}\text{C}$ for T-6 fuel indicate structural changes and also confirm the conductivity data. These curves may thus be used to evaluate structural changes in jet fuels. These changes may be prevented by using special additives or by blending with less viscous fuels. Figures 2; references 11 (Russian).

[308-12765]

UDC 665.63-103/405

FEATURES OF CHEMICAL COMPOSITION OF CRUDE OILS FROM OFF-SHORE AZERBAIJAN OIL DEPOSITS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 3, Mar 85 pp 31-33

SAMEDOVA, F. I., AGAYEVA, R. M., IBADZADE, A. D. and ALIYEVA, F. Z.,
Institute of Petrochemical Production imeni Yu. G. Mamedaliyev, AzSSR Academy of Sciences

[Abstract] Physical chemical characteristics are presented on crude oils from the 28 April and Darwin bank off-shore deposits. The oils were divided into 50°C fractions for detailed analysis. Despite its aromaticity, the Darwin bank crude contained fewer aromatic hydrocarbons in the 150° - 200°C and the 200° - 250°C fractions than those of 28 April. Adsorption separation over CaA zeolite of the naphthene-paraffin portion shows that n-aliphatic hydrocarbons were absent in all Darwin bank crudes and are present only in fractions, boiling below 300°C , of 28 April crudes, making the latter suitable for production without dewaxing. The iso-paraffin content in Darwin bank crudes boiling below 250° is much less than in the same fractions of 28 April. Naphthene hydrocarbons predominate in Darwin bank fractions boiling below 450°C . Ash from the Darwin bank crudes contains considerably more micro-elements such as nickel, magnesium and titanium than that of 28 April. References 4 (Russian).

[308-12765]

PERSPECTIVES FOR DEVELOPMENT OF PETROLEUM INDUSTRY IN GEORGIA

Moscow NEFTEKHIMIYA in Russian Vol 25, No 3, May-Jun 85 pp 292-296

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[Abstract] Petroleum has been known in Georgia for many centuries, harking back to the Greek-Persian wars. Modern exploitation of natural deposits goes back to 1929 when an Italian-Belgian group began drilling for oil, but the development was very slow up to 1970. Two primary centers are associated with the potential for more oil in Georgia: the first is in Kolkhid depression and Guryysh caving and the second in Kartliysk and Garekakhetsk depressions. Specific locations and geological formations are discussed here from the point of view of oil supply. An extensive program was developed for exploratory drilling during 1986-1990 period, especially aimed at deep deposits (below 5000 m). All Georgian oil has a characteristically low level of sulfur (about 0.5%). Georgian oils include naphtho-paraffinic, naphthenic and naphtho-aromatic components. References: 8 (Russian). [326-7813]

UDC 665.61

NEW PETROLEUMS FROM WEST KAZAKHSTAN

Moscow NEFTEKHIMIYA in Russian Vol 25, No 3, May-Jun 85 pp 297-304

NADIROV, N. K. and URAZGALIYEV, B. U., Institute of Petroleum and Natural Salts Chemistry, KazSSR Academy of Sciences, Gur'yev

[Abstract] The petroleum from new deposits in Western Kazakhstan may be subdivided into two groups: paleozoic petroleum from the areas close to the Caspian Sea (between Ural and Volga rivers) and petroleum from the peninsulas Buzash, Tyub-Karagan and Northern Ustyurt. Physical-chemical characteristics of these petroleum are tabulated by their place of origin. Most of the petroleum from these deposits in Western Kazakhstan are heavy and viscous, with low yield of the light fractions. Paleozoic petroleum from the Caspian Sea area are paraffinous and they contain larger fractions of light components. An equation is developed for the calculation of kinematic liquid viscosity as a function of density. Thus, in spite of the fact that petroleum is a complex solution of hydrocarbons, in this respect it acts as an individual hydrocarbon. Figures 3; references 5 (Russian, 2 by Western authors). [326-7813]

USE OF PHOTOCHEMICAL REACTIONS IN STUDYING CRUDE OILS

Moscow NEFTEKHIMIYA in Russian Vol 25, No 3, May-Jun 85 pp 310-314

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imeni P. G. Melikishvili, GSSR Academy of Sciences

[Abstract] There exists a growing need for new effective methods of studying crude oils which would expand our knowledge of their composition and properties and serve as an indicator for new synthetic approaches to these economically important products. Photochemical reactions were shown to be useful in studying reactions occurring during petroleum processing and during isolation of residual elements from petroleum and its products. Photocondensation of phenanthrenes with maleic anhydride was used to develop a method for investigating such hydrocarbons after isolation from high boiling petroleum fractions. A highly effective non-phytotoxic preparation was developed from inhibited mineral oil for the control of citrus fruit pests; its use led to increased harvest of tangerines by 18-22%.
References 19: 18 Russian, 1 Western.
[326-7813]

UDC 665.61.033.2:543[.544 + 51]

STUDY OF HYDROCARBONS FROM WEST SIBERIAN PETROLEUM

Moscow NEFTEKHIMIYA in Russian Vol 25, No 3, May-Jun 85 pp 315-321

MUSAYEV, I. A., KURASHOVA, E. Kh., SIMANYUK, R. N., POLYAKOVA, A. A.,
YERMAKOVA, L. S., SMIRNOV, M. B. and SANIN, P. I., Institute of Petrochemical
Synthesis imeni A. V. Topchiyev, USSR Academy of Sciences; All Union
Scientific Research Institute of Petroleum Processing

[Abstract] Hydrocarbon composition of the West Siberian petroleum fraction boiling in the range of 350-540°C was studied; it contained hydrocarbons with C₁₈-C₄₀ carbon atoms, 74% of which were in the range of C₂₁-C₃₀. Among the aromatic products, 60% were single ring compounds, containing normal, branched and isoprene type hydrocarbons as substituents. Saturated cyclic hydrocarbons were dehydrogenated and the aromatic products were analyzed showing certain analogy with the hydrocarbon composition in the originally isolated aromatic fraction; evidently there must be some genetic connection between these compounds. Condensed hydrocarbon systems containing cyclohexane and cyclopentane rings were isolated. References 6: 5 Russian, 1 Western.
[326-7813]

OXYGEN-CONTAINING COMPOUNDS IN CRUDE OIL FROM SAMOTLORSK DEPOSITS

Moscow NEFTEKHIMIYA in Russian Vol 25, No 3, May-Jun 85 pp 360-363

SAVINYKH, YU. V., IL'YUSHENKO, N. A., BASHLAY, O. E. and SIROTKINA, Ye. Ye.,
Institute of Petroleum Chemistry, Siberian Department, USSR Academy of
Sciences

[Abstract] Oxygen-containing components of crude oils are important compounds, yet they have been studied inadequately. In this paper, data are reported of quantitative analysis of ketones, free and bound acids and phenols obtained during fractional distillation of petroleum from Samotlorsk deposits. Ketones represent 50-80% of total oxygenated compounds; acids and phenols account for 1.5-3%. Total oxygen content in these petroleum samples was 0.3-0.4%. During thermal distillation process, the content of acids, phenols and ketones is increased even though total oxygen level remains the same; most probably this is due to thermal decomposition of simple ethers which then convert to above compounds. References 6: 4 Russian, 2 Western.
[326-7813]

CHEMICAL MODIFICATION OF POLYETHYLENE TEREPHTHALATE WITH DIHALOGEN-SUBSTITUTED TEREPHTHALIC ACIDS

Minsk VESTSI AKADEMII NAVUK BSSR: SERYYA KHIMICHNYKH NAVUK in Russian No 3,
May-Jun 85 (manuscript received 22 Apr 83) pp 83-85

BONDAREVA, O. M., LOPATIK, D. V., PROKOPCHUK, N. R., OSIPENKO, I. F.,
KHOKHRYAKOVA, N. A. and ARIKO, N. G., Institute of Physical-Organic Chemistry,
BSSR Academy of Sciences

[Abstract] A study was made of the modifying effect of dihalogen-substituted terephthalic acids on the physical and mechanical properties of polyethylene terephthalate fibers. 2,5-Dichloro- and 2,5-dibromoterephthalic acids, when used as modifiers in copolycondensation of terephthalic acid with ethylene glycol, have different effects on the physical and mechanical properties of resulting copolyester fibers. Polyethylene terephthalate fibers, modified with 1-7 mole % 2,5-dichloroterephthalic acid, have superior mechanical properties and higher glassification temperatures than non-modified fibers or fibers modified with 2,5-dibromoterephthalic acid. References 8: 7 Russian, 1 Western.
[321-12765]

REFORMING GASOLINE OVER CATALYST KR-104

Minsk VESTSI AKADEMII NAVUK BSSR: SERYYA KHIMICHNYKH NAVUK in Russian No 3, May-Jun 85 (manuscript received 27 Aug 84) pp 86-91

SEN'KOV, G. M., PUSHKAREV, V. P., KOZLOV, N. S., VARSHAVSKIY, O. M., PRYAKHINA, N. Ya., GLINCHAK, S. I. and GORBATSEVICH, M. F., Institute of Physical-Organic Chemistry, BSSR Academy of Sciences

[Abstract] KR-104 is a widely used domestic polymetallic (Pt, Re, Cd, Fe) catalyst for making high octane components of motor fuel. The start-up and performance results of this catalyst on a high capacity LK-6u unit have been presented previously. In the present work, a further study was made of the performance and regeneration characteristics of the catalyst during reforming of a broad cut gasoline fraction in a one million ton per year industrial unit for 45 months. In the first stage of regeneration, the catalyst was reduced at 768 K for 9 hours and then oxychlorinated. During the second stage, the KR-104 was first treated for 8 hours with a hydrogen-containing gas at 768 K and then cooled and blown through with nitrogen. No change in Pt or Re content was observed, although the Cd content dropped markedly after 11 months and then remained constant. The octane number of the catalyzate was 80.4 (motor method, without TEL) and the catalyst lost both activity and selectivity and had to be regenerated after 5 months. The poor performance of the catalyst and its drop in activity are attributed to the high moisture content in the system during the start-up period. Figures 3; references 10: 8 Russian, 2 Western. [321-12765]

UDC 665.658:665.73/753

CATALYTICALLY REFORMED GASOLINE FROM LIQUEFIED KANSK-ACHINSK COAL

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 7, Jul 85 pp 6-7

GLOZSHEYN, A. Ya., MARYSHEV, V. B., SHAPIRO, R. N., ZHARKOV, B. B., PETROV, Yu. I. and YULIN, M. K., All-Union Scientific Research Institute of Petrochemistry; Institute of Combustible Deposits

[Abstract] An analysis was conducted on catalytically reformed fractions (45-400°C) of gasoline derived from liquefaction of Kansk-Achinsk coal and from petroleum. The basic difference between the two types of gasoline was in the aromatic hydrocarbon levels, which were significantly higher in the coal-derived gasoline (21.6 vs. 12.3% by wt.). In addition, 2/3rds of the naphthenes in the coal-derived gasoline consisted of cyclohexane homologs, whereas in the gasoline reformed from crude cyclopentane homologs predominated. Figures 1; references 5 (Russian). [345-12172]

HYDROCARBON CONDENSATION PRODUCTS OF TURKMENISTAN GAS FIELDS AS MOTOR FUEL COMPONENTS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 7, Jul 85 pp 11-13

KUL'DZHAYEV, B. A., SERGIYENKO, S. R. and TSIBROVA, Ye. G., Institute of Chemistry, Turkmen SSR Academy of Sciences

[Abstract] Technical data are provided in tabular form on the composition of hydrocarbon condensation products obtained from various gas fields in Turkmenia, with an analysis of their usefulness as gasoline and diesel fuels. For example, high-paraffin condensates are characterized by low octane numbers (30-50) of the gasoline fraction (150-180°C). However, lowering the temperature at the end of distillation to 120-130°C increased the octane number to 73, one point higher than required by State Standards for automobile gasoline A-72. The cetane number of diesel fuels in general exceeded the State Standards, especially in the case of fractions 150°C and 180°C of the high-paraffin condensates obtained from the Shatlyk site.

Summarized data are presented on the suitability of the products obtained from the different site for the different types of fuels.

References 4 (Russian).

[345-12172]

UDC 665.644.26

SELECTIVE HYDROCRACKING OF LIGHT GASOLINE FRACTIONS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 7, Jul 85 pp 13-15

KOZLOV, I. T., KHAVKIN, V. A. and NEFEDOV, B. K., All-Union Scientific Research Institute of the Petroleum Industry

[Abstract] A novel approach has been developed for the production of high-quality automobile gasoline, which consists of a combination of hydrocracking of direct-distillate 65-105°C gasoline fraction and subsequent catalytic reforming. The catalyst of choice is a high-silicon zeolite with a $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 40-90. The catalyst, designed for selective deparaffinization of intermediate and high bp distillates, assures 100% conversion of n-decane in a mixture with aromatic hydrocarbons at 280-320°C under pressures to 4 MPa. Experimental trials demonstrated that greatest conversion was seen with normal C_6 - C_7 paraffins, resulting in an increase in C_6 - C_7 isoparaffins. The latter is also due to partial isomerization of the normal paraffins. The gaseous products consist largely of C_3 - C_4 compounds, while the yield of C_1 - C_2 compounds is less than 3 wt%. As a result of cracking of the normal paraffins, the octane number of the final products increases by 15-17.8 points, yielding gasoline with an octane rating of 73-77. Extensive testing of the catalyst have demonstrated their long-term

stability, suggesting possible utilization in commercial processes.
Figures 1; references 3 (Russian).
[345-12172]

UDC 66.067.1:66.5.765.404.038

FILTRATION OF MANNICH BASES THROUGH SOVIET FILTER AIDS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 7, Jul 85
pp 15-17

SKLYAR, V. Ya., RUDENKO, L. I., SKLYAR, V. T., GRECHKO, V. I. and
GARUN, Ya. Ye., Institute of Physical-organic Chemistry and Coal Chemistry,
Ukrainian SSR Academy of Sciences; Kremenchug Refinery; Drogobych Pilot
Plant of the All-Union Petrochemical Scientific Research Institute of
Planning and Construction

[Abstract] Trials were conducted to find Soviet substitutes for expensive foreign filter aids used in the filtration of Mannich bases for removal of mechanical impurities. The test results demonstrated that equivalent degrees of purity can be obtained with a mixture of 25% perlite + 25% kieselguhr + 50% sawdust, when filtration is performed under a pressure of 0.3 MPa and a temperature of 165-170°C. The end filtrate had a viscosity of 139-469 mm²/sec. The success of this method shows that it is possible to discontinue the use of the imported filter aids Zeolite-500 and Fibroflow for the purification of Mannich bases, and that one ton of the filtrate can be obtained with the use 0.32 kg less of the readily available Soviet filter aids than of the foreign products. Figures 1; references 3 (Russian).
[345-12172]

UDC 621.892.097.004.12:543.422

EFFECTS OF VIBRATION-INDUCED CAVITATION ON PHYSICOCHEMICAL CHARACTERISTICS OF AIRCRAFT FUEL

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 7, Jul 85
pp 23-25

MERTSALOV, P. P., BEDRIK, B. G. and SUPON'KO, K. L.

[Abstract] An analysis was conducted on the factors leading to vibration-induced cavitation in aircraft fuel, resulting from sudden changes in hydrostatic pressure and resultant variability in tensile stresses. The data demonstrated that both hydrodynamic and aircraft factors predisposed to maximum cavitation in the vibration range of 30 to 300 Hz and vibroacceleration of 10 to 30 g. The specific alterations in fuels TS-1 and T-6 consisted of

changes in the granulometric profile with an increase in the percentage of particles 1-5 μ in size and a decrease in the percentages of those in the 5 to 100 μ (most pronounced with the 15-100 μ fraction). Other changes included a decrease in fuel viscosity and thermal stability, and an increase in tar substances. Vibration is, therefore, an important factor to be considered in the formulation and testing of new aviation fuels. Figures 3; references 8 (Russian).
[345-12172]

UDC 665.55:547.26:661.78

DISTRIBUTION OF SULFUR COMPOUNDS AND METALLOPORPHYRINS IN WESTERN
KAZAKHSTAN OIL

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 7, Jul 85
pp 33-35

MAYER, V. V., YAG'YAYEVA, S. M., KOTOVA, A. V. and KORYABINA, N. M.,
Institute of Oil and Natural Salts Chemistry, Kazakh SSR Academy of Sciences

[Abstract] Tabular data are provided on the distribution of sulfur compounds and metalloporphyrin complexes among the oil deposits in Western Kazakhstan. Summarizing the information on sulfur compounds showed that Zhanazhol and Korolev deposits are classified as high in sulfur (2.02-2.65 wt% S), while the crude from Ul'kel'-Tyube is low in sulfur (0.41 wt% S). Other deposits in that part of the republic hold intermediate positions. Determinations of Ni and Va porphyrins demonstrated that the new oil from the Zhanazhol deposit is heavy in Va porphyrins (4.5-11.7 mg/100 g). Samples from the Tortay deposits have yielded both Ni and Va porphyrins, while Ul'kel'-Tyube yielded only Va porphyrin. High levels of Va porphyrin were also found in Korolev, Karasor and Ayrankul' deposits; none, however, was detected in the interfluvial Ural, Volga and Emba region. References 7 (Russian).
[345-12172]

UDC 615.015.1

RELATIONSHIP BETWEEN ELECTRONIC STRUCTURE AND TOXICITY OF 8-AZASTEROIDS

Minsk VESTSI AKADEMII NAVUK BSSR: SERYYA KHIMICHNYKH NAVUK in Russian No 3, May-Jun 85 (manuscript received 15 Nov 84) pp 78-82

SOKOLOV, Yu. A., GOLUBOVICH, V. P., KUZMITSKIY, B. B. and AKHREM, A. A.,
Institute of Bioorganic Chemistry, BSSR Academy of Sciences

[Abstract] A study was made of the relationship to toxicity to the distribution of electron densities in 21 8-azasteroids compounds. By employing the Hückel extended quantum-chemical method, two equations were derived which give theoretical results that agree well with experimental data:

$LD_{50} = 14.722 - 3.619P_2$ ($m=1$) and $LD_{50} = 12.138 - 5.369P_3$ ($m=2$), where P_2 and P_3 are the electron densities at atoms 2 and 3, respectively.

References 12: 8 Russian, 4 Western.

[321-12765]

UDC 541.64.954

LIMIT VALUES OF SOLID-PHASE CYCLIZATION OF POLYAMIDO ACIDS

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 283, No 1, Jul 85
(manuscript received 12 Jul 84) pp 133-135

MIKITAYEV, A. K., BERIKETOV, A. S., KUASHEVA, V. B., ORANOVA, T. I. and
TAOVA, A. Zh., Kabardino-Balkar State University, Nal'chik

[Abstract] Studies were conducted on the maximum possible degree of cyclization of polypyromellitimide catalyzed by imidazole since, in theory, such cyclodehydration reactions can proceed to 100% completion. Reactions carried out over a temperature range of 573-623°K showed 82% cyclization without the catalyst and 90% cyclization with the catalyst. Analysis of plots relating the temperature of glassy transition with the degree of cyclization and determination of the temperature corresponding to the onset of thermal destruction, demonstrated that 100% cyclization would result in a product with an onset of destruction at 923°K. Consequently, approximation of 100% cyclization would result in a thermally superior polyamide. Solid-phase techniques necessary to achieve the desired degree of cyclization would require the use of low MW additives, small temperature intervals for cyclization, and acceleration of the reaction rate. Figures 3; references 5 (Russian).
[340-12172]

UDC 541.12.034.2

ENERGY FUNCTION AND CONDUCTIVITY OF METAL-POLYMER COMPOSITES

Minsk VESTSI AKADEMII NAVUK BSSR: SERYYA KHMICHNYKH NAVUK in Russian No 3, May-Jun 85 (manuscript received 25 Sep 84) pp 105-106

KHITROVA, O. N., DANYUSHINA, A. M., MARDASHEV, Yu. S. and YEROFEYEV, B. V., Moscow State Pedagogic Institute imeni V. I. Lenin; Institute of Physical-Organic Chemistry, BSSR Academy of Sciences

[Abstract] The work function of electrons from polymer or metal as a function of electrical conductivity at the percolation zone was studied in two

series of composites. In the first series (Zn + polyethylene), the metal was varied, and in the second (Zn + polyethylene, polyvinyl alcohol, polytetrafluoroethylene), the polymer was varied. The rise in conductivity of the composite is shown to vary with the work function of the polymer, which is apparently related to the transfer mechanism. The conductivity of the composite is thus determined by the nature of the dielectric (polymer). Figures 2; references 5 (Russian).
[321-12765]

UDC 541.141

RATE OF INITIATION OF PHOTOPOLYMERIZATION OF LIQUID OLIGOMER COMPOSITIONS

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 7, Jul 85
(manuscript received 30 Nov 83) pp 764-768

KARANAUKH, A. P., GUDZERA, S. S. and VERBOVAYA, S. N., Institute of High Molecular Weight Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] A mathematical analysis was conducted on the photopolymerization of α,ω -acryl-(bis-propyleneglycol)-2,4-toluene dicarbamate with diacetyl as initiator, to assess the relationship between the rate of photopolymerization and the concentration of the initiator in a film of infinitely small thickness. Comparison of the experimental data obtained with and without a strong inhibitor of photopolymerization demonstrated that the rate was directly proportional to the square root of the initiator concentration. The rate obtained with the inhibitor represents an average value related to film thickness, and does not represent the actual course of the reaction. References 9: 6 Russian, 3 Western.
[341-12172]

UDC 678.746:744.339-13

GRAFT POLYMERIZATION OF ETHYLENE GLYCOL MONOMETHACRYLATE TO POLYVINYLPIRROLIDONE

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 51, No 7, Jul 85
(manuscript received 23 Mar 84) pp 767-769

VOROB'YEV, A. A., SUBERLYAK, O. V., SOSHKO, A. I. and KURYLO, M. S., Lvov Polytechnic Institute

[Abstract] Kinetic studies were conducted on thin-layer (1 mm) graft polymerization of ethylene glycol monomethacrylate (EGM) to polyvinylpyrrolidone (PVP), in order to provide further improvement in materials available for soft contact lenses, biological membranes, endoprostheses, etc. The studies conducted with ca. 11,000 MW PVP with either benzoyl

peroxide or azobisisobutyrate dinitrile as initiator showed that the reaction followed standard graft polymerization kinetics, for which an equation was derived. The polymerization was greater than unity in terms of the EGM monomer and greater than 0.5 in initiator. These parameters were interpreted to indicate that chain rupture involved primary radical and PVP radicals. For the preparation of copolymers containing 9-11% PVP, elevated polymerization temperatures (85-90°C) were required. Figures 2; references 6: 3 Russian, 3 Western.
[341-12172]

UDC 547.466.1+547.466

ADDITION OF N-PROTECTED AMINO ACIDS TO CHLOROMETHYLATED COPOLYMER OF BUTADIENE AND METHYLSTYRENE

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 28, No 6, Jun 85
(manuscript received 26 Dec 83) pp 88-90

VASILYEV, V. N., ZVONKOVA, Ye. N. and YEVSTI, R. P., Chair of Chemistry and Technology of Fine Organic Compounds, Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov

[Abstract] A series of diene copolymers with styrene and methylstyrene was studied and the chloromethylated copolymer of butadiene and methylstyrene is proposed as a polymer matrix for the synthesis of peptides. The degree of "setting" of an anchoring amino acid was evaluated quantitatively with the utilization of various salt forming agents (triethylamine, Li, Na, K, Cs, and Rb). The triethylamine salts of N-protected amino acids (tertiary-butyloxycarbonyl-leucine-OH and (carbobenzoxy)benzyloxycarbonyl-glycine-OH) when reacted with the chloromethylated polymer did not give a high degree of conversion even with an excess of triethylamine. The content of amino acid was .094-4.42 mmole/g polymer. The use of alkali metal salts of the N-protected amino acids increased the yield of polymer esterified amino acids significantly (up to 28.78 for Cs). It was discovered that the nature of the amino acid (glycine, alanine, leucine), and of the N-protecting grouping, influence the degree of binding of the N-protected amino acid. When chloromethylated polymer with a high chlorine content (7.30%) in the form of a highly swollen gel is used, the degree of "setting" of the amino acid for the polymer rises proportionally to the increase in the quantity of chloromethyl groups and the amino acid content was up to 65.13 mmole/g polymer for the Cs salt. References 8: 3 Russian, 5 Western.
[342-12886]

EFFECT OF CONDITIONS FOR OBTAINING SUSPENSION POLYVINYLFLUORIDE ON ITS MOLECULAR WEIGHT

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 28, No 6, Jun 85 (manuscript received 16 Jan 84) pp 91-94

SIRLIBAYEV, T. S., KALYADIN, B. G. and TIRKASHEV, I., Chair of General Chemistry, Tashkent State University imeni V. I. Lenin

[Abstract] The influence of such parameters as the nature of the stabilizer for the suspension and its concentration in the aqueous phase, the rate and integral dose of irradiation, and the ratio of the monomer to the aqueous phase on the molecular weight (MW) of samples of polyvinylfluoride (PVF) obtained by radiative suspension polymerization of vinyl fluoride (VF) was studied. VF polymerizations were initiated with γ -rays of ^{60}Co at dose rates of 0.2-1.5 Gr/sec at 293°K with initial stabilizer amounts of 0.01-2.5% by wt. in the aqueous phase using seven different stabilizers. For the stabilizers Solvar (polyvinyl alcohol containing 17% non-saponifying acetate groups) and carboxymethylcellulose, the MW of PVF decreased as the concentration of the stabilizer increased in the aqueous phase; for methylcellulose and acetylcellulose the molecular mass remained practically unchanged, and for the copolymers of maleic acid with acrylamide and with acrylic acid and for the ammonium salt of the copolymer of maleic acid with acrylic acid and the MW increased. Varying the initial ratio of VF to aqueous phase from 1:1 to 1:7 showed that up to 1:3 the viscosity and molecular wt. increase and then they decrease. With an increase of the integral dose of irradiation the MW increases because of the flow of the suspension polymerization of VF in heterophase conditions. The number of factors and the degree of their influence on the molecular wt. are noticeably greater for radiative suspension polymerization than for polymerization in mass. The study, to some degree, allows the effective regulation of the MW of the synthesized polymers and some of their properties. References 13: 11 Russian, 2 Western.
[342-12886]

UDC 678.024.8

STUDY OF PROCESS FOR OBTAINING FINELY DIVIDED RUBBER POWDER BY GRINDING
VULCANIZED RUBBER SCRAP WITH ABRASIVE TOOL

Moscow KAUCHUK I REZINA in Russian No 5, May 85 pp 4-5

MOROZENKO, V. N., GORDIYENKO, N. A., YASEV, A. G. and PROVOLOTSKIY, A. Ye.

[Abstract] Spent rubber is currently re-cycled by mechanical shredding in a rolling mill to 0.6-1.0 mm particle size. This is too large for use as filler material in rubber mixtures without additional treatment. In the present work, data was obtained from an experimental rotary abrasive device operating at 0.05-0.8 mm per revolution cutting speed, 30-50 m/sec rotational velocity and 75-140 kN/m grinding force. After processing the data with an ES-1020 computer, formulas were developed which may be used to compute engineering parameters for economical grinding of vulcanized scrap rubber (tire casings). Productivity of grinding is shown to be a function of the rotational speed of the abrasive wheel and the feed rate of the rubber. Efficiency may be increased by raising the rotational speed. Figure 1; references 4 (Russian).

[296-12765]

UDC 678.023.3

DEVELOPING CONDITIONS FOR MAKING TIRE TREAD MIXTURES FROM GRANULATED
NATURAL RUBBER

Moscow KAUCHUK I REZINA in Russian No 5, May 85 pp 6-8

GOL'MAN, A. M., GINZBURG, L. R., GRISHIN, B. S. and SAPRONOV, V. A.

[Abstract] Natural rubber (baled) must first be masticated before it can be blended with rubber mixtures. Since this is a costly step both in energy and labor, a comparative study was made using bales of SMR-5 and granulated (2-3 mm particle size) natural rubber obtained from the Malay Association of Natural Rubber Producers to make tire tread rubber mixtures in a laboratory mill. The study showed that by using the granulated rubber, the process may be intensified and a 40% saving in electrical energy realized. Figures 2; references 8: 6 Russian, 2 Western.

[296-12765]

REPROCESSING WASTES FROM LATEX PRODUCTION AND USING THEM FOR FOAM RUBBER

Moscow KAUCHUK I REZINA in Russian No 5, May 85 pp 8-9

MAZINA, G. R., NESYNOVA, R. A., SLEPNEVA, V. N. and PELINA, Zh. V.

[Abstract] Unfilled mixtures containing 85-95% uncured rubber are used in latex production, so that utilization of any waste constitutes a considerable savings in material resources. Wastes are made up of non-vulcanized and vulcanized groups, the latter having the largest volume. A study shows that these vulcanized wastes can be recovered, crushed, screened, dispersed in water and re-cycled as latex mix to be combined with serially produced latex to make foam rubber. Figure 1; references 4 (Western).
[296-12765]

STUDY OF PHASE COMPOSITION AND STRUCTURE OF POLYMER MIXTURES BASED ON SKEPT-50

Moscow KAUCHUK I REZINA in Russian No 5, May 85 pp 10-12

KOMAROV, S. A., PISKUNOVA, Ye. Ye., KOLESNIKOV, A. A. and KULEZNEV, V. N.

[Abstract] A study was made of the phase composition and structure of polymer mixtures of SKEPT-50 (an ethylene-propylene synthetic elastomer) and chlorosulfonated polyethylene (KhSPE); butadiene-nitrile (SKN-40), chloroprene (nairite KR) and alpha-methylstyrene (SKMS-30 ARK) rubbers; and high pressure polyethylene (PEVD). Calorimetric curves (-123° to $+77^{\circ}\text{C}$) for the mixtures show two alpha relaxation transitions. Structure data, obtained by X-ray analysis, and phase composition, determined by differential scanning calorimetry, show that two types of structure are possible. If the SKEPT-50 content is below 40-50% (by weight), the surface layer is composed chiefly of SKEPT-50 copolymer, while the bulk consists of SKEPT-50 dispersed in PEVD. Above 50% copolymer content, a microemulsion of SKEPT-50 in PEVD is contained between layers of SKEPT-50 (continuous phase). The type of phase structure resulting from polymer mixtures and the distribution of components in the bulk and at the surface layer is a function of viscosity, elasticity, surface tension of the components, temperature, shear stresses and adhesion interactions in the mixing zone. Figures 3; references 8: 6 Russian, 2 Western.
[296-12765]

STUDY OF INHIBITING ACTIVITY OF OLIGOMERIC THIOPHOSPHONIC ACID DIAMIDES

Moscow KAUCHUK I REZINA in Russian No 5, May 85 pp 13-14

SARAYEVA, V. P., ZHDANOVA, A. N., KITSENKO, A. V. and BEBIKH, G. F.

[Abstract] Addition of high and low molecular weight inhibitors to butyl rubbers increases their heat resistance and gives them special properties such as gas-impermeability and high elasticity. A study was made of the effectiveness of oligomeric thiophosphonic acid diamides (OI-1 and OI-2) as inhibitors of thermo-oxidative breakdown of butyl rubber at 200°-240°C in air and compared with an industrial low molecular weight inhibitor, Polygard. Effectiveness was determined by comparing the intrinsic viscosities. As the temperature was increased, the intrinsic viscosity of the oligomer-inhibited rubbers dropped at a lower rate than that of the Polygard. Also, the breakdown rate of the Polygard-inhibited rubbers increased rapidly with temperature, while that of the OI-1 and OI-2 inhibitors remained unchanged. Relative effectiveness of the oligomeric inhibitors was observed to increase about 7-fold with rising temperatures to 240°C. IR-spectra show an absence of hydroxyl or carbonyl groups in the oxidized rubber, indicating a depolymerizing reaction owing to rupture of C-C bonds. The products of the thermal breakdown of the inhibitors are evidently capable of re-welding the butyl rubber macromolecules and thereby decreasing the depolymerization rate. Thus, OI-1 and OI-2 inhibitors exhibit higher activity at 200°-240°C than that of Polygard. Figures 3; references 8: 7 Russian, 1 Western. [296-12765]

RESISTANCE TO FAILURE OF ELASTIC MATERIALS, CURED ONTO RIGID SUBSTRATE

Moscow KAUCHUK I REZINA in Russian No 5, May 85 pp 14-17

ZUYEV, Yu. S., KOMOLIKOVA, A. P., SMYSLOVA, R. A. and KHOTIMSKIY, M. N.

[Abstract] A study was made of factors leading to strengthening or weakening of elastomers when applied by curing onto a rigid substrate of metal or glass. The chief factors are limitation of deformation and tendency towards molecular orientation. Tests were run on synthetic rubber samples ranging from 20,000 to 300,000 molecular weight. Strengthening effect was evaluated from the coefficient of tensile strength of the adhered rubber to that in the free state, $K_T = T_p/T_s$. If $K_T > 1$, strengthening was observed; if $K_T < 1$, weakening resulted. Resistance to failure (ripping, tearing) may either increase or decrease, depending on whether the strengthening effects of increased hardness from curing, or the weakening effect of inhibition of molecular orientation predominate. Strengthening is also facilitated by

low molecular weight of the initial elastomer, an increase in its hardness and by strengthening of the adhesion bond between the elastomer and the substrate. Strengthening decreases with increasing molecular weight and may result in failure with insufficient hardness. Figures 4; references 12: 10 Russian, 2 Western.
[296-12765]

UDC 678.7-1.742.3.065

ALTERING MECHANICAL PROPERTIES OF RUBBER BY FILLING WITH POLYPROPYLENE

Moscow KAUCHUK I REZINA in Russian No 5, May 85 pp 18-19

VETOSHKINA, Z. V. and NIKITINA, O. B.

[Abstract] Results are presented of a study of the physical and mechanical properties of SKI-3 vulcanizates containing isotactic polypropylene (PP) and technical grade carbon black P514. The ingredients were combined in accordance with a standard recipe for tire casings (GOST 23785.7-79) and mixed in a rubber blender at 170°-180°C. The results show that while PP increases the modulus of elasticity significantly, shredding resistance drops unless carbon black is also present. When both are present, the modulus of elasticity is higher than that of serially produced vulcanizates. Thus, the combined use of PP and carbon black makes it possible to raise both the modulus of elasticity and the resistance to shredding of vulcanizates without adding nitroso-aniline modifiers such as resotropin or nitrol. References 5 (Russian).
[296-12765]

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METHODICAL APPROACH TO EVALUATING PROPERTIES OF RUBBERS, TAKING INTO ACCOUNT NATURE OF DEFORMATION IN TIRES

Moscow KAUCHUK I REZINA in Russian No 5, May 85 pp 30-32

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[Abstract] Working temperature is one of the most important criteria of dependability in pneumatic tires, especially the super-sized 14.00-20 model Bel-67 used on self-propelled cranes (65 km/hr speed at high initial pressure and 54 kN tire load). Stationary tests under simulated working conditions show that even after 30 minutes rolling, both tire temperature and rate of heat build-up exceed allowable values, and fatigue endurance diminishes rapidly. In the present work a laboratory method was developed for evaluating the properties of tire treads and the deformation conditions characteristic

for such tires under working conditions so that correct rubber compositions may then be selected which will provide the needed complex of properties (heat build-up, wear resistance, fatigue endurance) in the tires.

Figures 3; references 6: 5 Russian, 1 Western.

[296-12765]

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KINETICS OF DESTRUCTION OF BUTYL RUBBER IN POLYTHERMAL AND ISOTHERMAL CONDITIONS

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 26, No 3, May-Jun 85 (manuscript received 3 Feb 84) pp 320-323

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[Abstract] Studies of the kinetics of destruction of butyl rubber containing 0.5% high molecular wt. oligomer inhibitors OI-1A and OI-4A, compounds similar to those described by the authors in reference 1, were carried out isothermally at 200, 220 and 240°C for up to 120 minutes and polythermally from room temperature to 500°C. The effectiveness of the oligomer inhibitors to reduce thermal oxidation was compared to butyl rubber samples with 0.5% polygard, a commercial low molecular inhibitor. The rate constant for the destruction of butyl rubber with 0.5% polygard at 200-240°C is 2-4 times greater than that for the oligomer stabilized samples. As temperature is increased, the coefficient of destruction of samples containing oligomers does not increase significantly, but for polygard it increases 8-10 times. The energy of activation of oxidation for the oligomer stabilized samples is greater than for the polygard controls. These data confirm the greater inhibiting activity of the oligomers. The relative effectiveness of these polyfunctional inhibitors is 3-7 times greater than for polygard at 200-240°C. Thermographs made at various heating rates from room temperature to 500°C also demonstrated high effectiveness of the oligomer inhibitors. Activation energy for thermal oxidation agrees well in isothermal and polythermal conditions for the inhibitors. IR spectra established that, during thermal oxidative destruction, oxygen forming compounds are not formed and the limiting process for the degradation is the breaking of the C-C bond. Significant reduction of thermal oxidative destruction of butyl rubber with oligomer inhibitors and preservation of its molecular weight demonstrates the polyfunctional capability and high inhibiting activity of these new oligomer inhibitors. Correlation of the activation energy in isothermal and polythermal conditions confirms the reliability of the results. Figures 4; references 8: 5 Russian, 3 Western.

[343-12886]

STUDY OF PROCESS OF BIOLOGICAL TREATMENT OF WASTE EFFLUENTS

Moscow KAUCHUK I REZINA in Russian No 5, May 85 pp 35-38

MAKEYEVA, Ye. N., GOREMYKINA, L. F., SHLYGINA, G. S. and ULANOVSKAYA, A. P.

[Abstract] In the production of synthetic rubber by emulsion polymerization, large amounts of water are used (100 cu.m. per ton of production) which creates pollution problems. Biological treatment appears to be the most cost-effective (4 kopecs per cu.m.). However, this requires that the emulsifiers used can undergo biodegradation and a study was made of the biodegradation of non-ionogenic emulsifiers OKS-1 and synthanol DS-10, and polyethylene glycol PEG-9 in concentrations ranging from 1 to 500 mg/liter in aeration tanks. The results show that synthanol DS-10 is readily biodegradable and a maximum permissible concentration of 50 mg/liter in the effluent with 12 hours aeration is thereby recommended. However, emulsifiers prepared from hydroxyethylated C₁₇-C₁₈ fatty alcohols and primary C₁₇-C₂₀ alcohols are non-biodegradable under standard conditions and are not recommended. PEG-9 is capable of total biochemical breakdown after a 7-8 week period of microflora adaptation to the sludge. Under these conditions, and 12 hours aeration with 3-3.5 g/liter of active sludge, the maximum permissible concentration of PEG-9 is 100 mg/liter. References 9: 7 Russian, 2 Western.
[296-12765]

MISCELLANEOUS

UDC 666.233:621.921

SYNTHESIS OF DIAMONDS FROM CARBOHYDRATES

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 6, Jun 85
(manuscript received 26 Mar 84) pp 1517-1518

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[Abstract] Standard diamond synthesis from hydrocarbons uses pressures of 120-130 kbar and temperatures of 2000°C or higher. The current work indicated that carbohydrates without the addition of metallic catalysts can form diamonds in the region of their stability under unspecified, though less severe conditions maintained for a period of 30-45 s. Yields averaged 60% and ranged up to 90%, with grain size of 5-80 μ . The diamonds were predominantly light green, though some individual crystals were yellow to white. They were stable in air up to 770°C. Figures 2; references 4: 3 Russian, 1 Western.
[335-12672]

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